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(54) **DETERGENTS POUR LAVE-VAISSELLE CONTENANT DES PHOSPHATES SPECIAUX**

(54) **MACHINE DISHWASHING COMPOSITIONS COMPRISING SPECIAL PHOSPHATES**

(57) Machine dishwashing detergents have advantages in terms of hydrolytic stability, storage stability, and performance if they contain phosphates with nitrogen cations, especially pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate.

Abstract

Machine dishwashing detergents have advantages in terms of hydrolytic stability, storage stability, and performance if they contain phosphates with nitrogen cations, especially pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate.

MACHINE DISHWASHING COMPOSITIONS COMPRISING SPECIAL PHOSPHATES

Field of the Invention

The present invention relates to detergents for machine dishwashing which comprise phosphate builders.

Background of the Invention

Phosphates have long been known as builders in laundry detergents and cleaning products and have advantages such as good complexing properties for heavy metals and water hardeners, and support the cleaning performance. Whereas in textile detergents builder combinations based on zeolites and/or silicates have in part become established, phosphates continue to be the most important builders in the field of the machine washing of tableware and kitchenware.

The industrially most important phosphate and that most widespread in the field of detergents is sodium triphosphate, correctly called pentasodium triphosphate. It occurs in two anhydrous crystalline forms and one hydrated form. Of the crystalline forms, one is termed "phase II", which is the low temperature form, whereas the "phase I" triphosphate is stable at temperatures above the transformation temperature (approximately 420°C). In addition to sodium phosphates, the most expensive potassium phosphates also possess a certain significance since they are more readily soluble and more active.

A problem which occurs when phosphates are used in dishwashing compositions is the loss of activity on storage. Within the compositions and during use, the known phosphates suffer hydrolysis to a greater or lesser extent depending, inter alia, on the storage temperature and on the water content and the pH of the compositions. Irrespective of the form in which they

are presented, machine dishwashing compositions cannot be produced entirely free of water on the industrial scale, with the consequence that it is necessary to accept a certain loss of phosphate activity. While in the case of solid commercial forms such as powders, granules, extrudates, flakes, pellets or tablets hydrolysis may be tolerated on the part of the formula, it is a distinct problem in the case of liquid or gel presentation forms and adversely affects the storage stability of the compositions. In liquid formulations, however, the addition of water is often unavoidable in order to allow the action of thickeners, which may in turn be necessary for the purpose of stabilizing against sedimentation.

It is an object of the present invention to provide phosphate builders which can be incorporated like the known builders into machine dishwashing compositions irrespective of their presentation form. The builders to be provided ought to possess a relatively high hydrolytic stability and ought overall to give the compositions greater storage stability and performance advantages. In particular, it ought to be possible to incorporate the builders into liquid machine dishwashing compositions without hydrolysis problems even if the compositions are to be water based.

Summary of the Invention

It has now been found that phosphates containing nitrogen cations have advantageous properties as builders for machine dishwashing compositions.

The invention provides compositions for the machine washing of tableware and kitchenware, comprising phosphate(s) and, optionally, further detergent ingredients, at least one of the phosphates present in the compositions containing nitrogen cations.

Detailed Description of the Invention

In the context of the present invention, the term "nitrogen cations" characterizes positively charged ions which comprise at least one nitrogen atom. In this context it is possible to use, in principle, all cations containing nitrogen. Cations in which the positive charge has been produced by protonating or quaternizing a nitrogen atom are preferred. The positive charge of the nitrogen cations may be single or multiple, the singly positively charged cations being preferred in particular alongside the doubly positively charged ions.

A phosphate containing nitrogen cations may comprise further cations. In addition to the so-called "acid" salts, which still contain acidic hydrogen atoms, salts having a plurality of different cations may also be used in the context of the present invention. In the case of the ammonium ion as an example of a nitrogen cation, for example, the ammonium phosphates are suitable in accordance with the invention:

Ammonium phosphates is the collective term for the ammonium salts of the various phosphoric acids. The three orthophosphates give off NH_3 on heating to become polyphosphoric acid.

Primary ammonium phosphate (ammonium dihydrogen phosphate), $NH_4H_2PO_4$, is obtained when aqueous ammonia is neutralized with phosphoric acid until methyl orange just changes from yellow to red. It forms colorless, water-soluble crystals.

Secondary ammonium phosphate (diammonium hydrogen phosphate), $(NH_4)_2HPO_4$, is obtained in the form of colorless, readily water-soluble crystals as a coarsely crystalline precipitate when NH_3 gas is passed into a cooled solution of primary ammonium phosphate.

Tertiary ammonium phosphate (triammonium phosphate), $(NH_4)_3PO_4 \cdot 3H_2O$, is obtained by the action of gaseous

ammonia on the secondary phosphate; however, it is unstable in the solid state and breaks down with the release of NH_3.

Ammonium polyphosphates [$(NH_4PO_3)_n$ where n = 20-1000, MW approximately 2000-100,000] are obtained by careful condensation of the orthophosphates in an NH_3 atmosphere at 200-400°C. The polyphosphates are white, weakly acidic, water-insoluble products.

Instead of hydrogen, ammonium phosphates that may be used in accordance with the invention may also contain alkali metals, especially sodium and/or potassium, or other nitrogen cations or mixtures thereof.

However, it is advantageous if the phosphate containing nitrogen cations contains exclusively such cations. In this case it is possible either to synthesize salts from phosphate anions and different nitrogen cations or to use single-order salts composed only of one variety of cations and phosphate anions. The latter are preferred in accordance with the invention. Preferred compositions in the context of the present invention are those wherein at least one of the phosphates present in the compositions contains exclusively nitrogen cations.

In addition to the phosphates with nitrogen cations, the compositions of the invention may comprise further phosphates. Among the large number of commercially available phosphates, the greatest significance in the detergents industry is possessed by the alkali metal phosphates, with particular preference being given to pentasodium and pentapotassium triphosphate (sodium and potassium "tripolyphosphate").

Alkali metal phosphates is the collective term for the alkali metal (especially sodium and potassium) salts of the various phosphoric acids, among which meta-

phosphoric acids $(HPO_3)_n$ and orthophosphoric acid H_3PO_4, in addition to higher-molecular-mass representatives, may be distinguished. The phosphates combine a number of advantages: they act as alkali carriers, prevent limescale deposits on machine components, and lime incrustations on fabrics, and additionally contribute to cleaning performance.

Sodium dihydrogen phosphate, NaH_2PO_4, exists as the dihydrate (density 1.91 g cm^{-3}, melting point 60°) and as the monohydrate (density 2.04 g cm^{-3}). Both salts are white powders of very ready solubility in water which lose the water of crystallization on heating and undergo conversion at 200°C into the weakly acidic diphosphate (disodium dihydrogen diphosphate, $Na_2H_2P_2O_7$) and at the higher temperature into sodium trimetaphosphate ($Na_3P_3O_9$) and Maddrell's salt (see below). NaH_2PO_4 reacts acidically; it is formed if phosphoric acid is adjusted to a pH of 4.5 using sodium hydroxide solution and the slurry is sprayed. Potassium dihydrogen phosphate (primary or monobasic potassium phosphate, potassium biphosphate, PDP), KH_2PO_4, is a white salt with a density of 2.33 g cm^{-3}, has a melting point of 253°C [decomposition with formation of potassium metaphosphate $(KPO_3)_x$], and is readily soluble in water.

Disodium hydrogen phosphate (secondary sodium phosphate), Na_2HPO_4, is a colorless, crystalline salt which is very readily soluble in water. It exists in anhydrous form and with 2 mol (density 2.066 g cm^{-3}, water loss at 95°C), 7 mol (density 1.68 g cm^{-3}, melting point 48°C with loss of 5 H_2O), and 12 mol of water (density 1.52 g cm^{-3}, melting point 35°C with loss of 5 H_2O), becomes anhydrous at 100°C, and if heated more severely undergoes transition to the diphosphate $Na_4P_2O_7$. Disodium hydrogen phosphate is prepared by neutralizing phosphoric acid with sodium carbonate

solution using phenolphthalein as indicator. Dipotassium hydrogen phosphate (secondary or dibasic potassium phosphate), K_2HPO_4, is an amorphous white salt which is readily soluble in water.

Trisodium phosphate, tertiary sodium phosphate, Na_3PO_4, exits as colorless crystals which as the dodecahydrate have a density of 1.62 g cm^{-3} and a melting point of 73-76°C (decomposition), as the decahydrate (corresponding to 19-20% P_2O_5) have a melting point of 100°C, and in anhydrous form (corresponding to 39-40% P_2O_5) have a density of 2.536 g cm^{-3}. Trisodium phosphate is readily soluble in water, with an alkaline reaction, and is prepared by evaporative concentration of a solution of precisely 1 mol of disodium phosphate and 1 mol of NaOH. Tripotassium phosphate (tertiary or tribasic potassium phosphate), K_3PO_4, is a white, deliquescent, granular powder of density 2.56 g cm^{-3}, has a melting point of 1340°C, and is readily soluble in water with an alkaline reaction. It is produced, for example, when Thomas slag is heated with charcoal and potassium sulfate. Despite the relatively high price, the more readily soluble and therefore highly active potassium phosphates are frequently preferred in the cleaning products industry over corresponding sodium compounds.

Tetrasodium diphosphate (sodium pyrophosphate), $Na_4P_2O_7$, exists in anhydrous form (density 2.534 g cm^{-3}, melting point 988°C, 880°C also reported) and as the decahydrate (density 1.815-1.836 g cm^{-3}, melting point 94°C with loss of water). Both substances are colorless crystals which dissolve in water with an alkaline reaction. $Na_4P_2O_7$ is formed when disodium phosphate is heated at > 200°C or by reacting phosphoric acid with sodium carbonate in stoichiometric ratio and dewatering the solution by spraying. The decahydrate complexes heavy metal salts and water hardeners and therefore

reduces the hardness of the water. Potassium diphosphate (potassium pyrophosphate), $K_4P_2O_7$, exists in the form of the trihydrate and is a colorless, hygroscopic powder of density 2.33 g cm^{-3} which is soluble in water, the pH of the 1% strength solution at 25°C being 10.4.

Condensation of NaH_2PO_4 or of KH_2PO_4 gives rise to higher-molecular-mass sodium and potassium phosphates, among which it is possible to distinguish cyclic representatives, the sodium and potassium metaphosphates, and catenated types, the sodium and potassium polyphosphates. For the latter in particular a large number of names are in use: fused or calcined phosphates, Graham's salt, Kurrol's and Maddrell's salt. All higher sodium and potassium phosphates are referred to collectively as condensed phosphates.

The industrially important pentasodium triphosphate, $Na_5P_3O_{10}$ (sodium tripolyphosphate), is a nonhygroscopic, white, water-soluble salt which is anhydrous or crystallizes with 6 H_2O and has the general formula $NaO-[P(O)(ONa)-O]_n-Na$ where n = 3. About 17 g of the crystalline anhydrous salt dissolve in 100 g of water at room temperature, at 60°C about 20 g, at 100°C around 32 g; after heating the solution at 100°C for two hours, about 8% orthophosphate and 15% diphosphate are produced by hydrolysis. For the preparation of pentasodium triphosphate, phosphoric acid is reacted with sodium carbonate solution or sodium hydroxide solution in stoichiometric ratio and the solution is dewatered by spraying. In a similar way to Graham's salt and sodium diphosphate, pentasodium triphosphate dissolves numerous insoluble metal compounds (including lime soaps, etc). Pentapotassium triphosphate, $K_5P_3O_{10}$ (potassium triphosphate), is commercialized, for example, in the form of a 50% strength by weight solution (> 23% P_2O_5, 25% K_2O). The potassium

polyphosphates find broad application in the laundry detergents and cleaning products industry. There also exist sodium potassium triphosphates, which may likewise be used for the purposes of the present invention. These are formed, for example, when sodium trimetaphosphate is hydrolyzed with KOH:

$$(NaPO_3)_3 + 2\ KOH \rightarrow Na_3K_2P_3O_{10} + H_2O$$

They can be used in accordance with the invention in precisely the same way as sodium triphosphate, potassium triphosphate, or mixtures of these two; mixtures of sodium triphosphate and sodium potassium triphosphate, or mixtures of potassium triphosphate and sodium potassium triphosphate, or mixtures of sodium triphosphate and potassium triphosphate and sodium potassium triphosphate, may also be used in accordance with the invention.

In the context of the present invention it is preferred for the proportion of the abovementioned phosphates without nitrogen cations, based on the total amount of phosphates, to be kept low, for example, below 50% by weight, preferably below 25% by weight, and in particular below 10% by weight, based in each case on the total amount of phosphates. Compositions wherein all of the phosphates present contain nitrogen cations are particularly preferred.

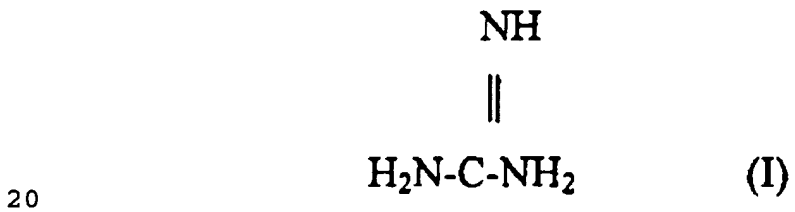
With this embodiment of the present invention as well it is preferred to use phosphates containing exclusively nitrogen cations. Compositions wherein all of the phosphates present contain exclusively nitrogen cations are therefore particularly preferred.

Suitable nitrogen cations in the phosphates present in the compositions of the invention, in accordance with

the invention, are cations which contain nitrogen atoms. It is preferred if the positive charge is induced by protonation or quaternization of the nitrogen atom. Accordingly, the following ions are particularly preferred cations in the phosphates:

Ammonium (NH_4^+), hydrazinium ($H_2N-NH_3^+$), iminium ($R^1-C(R^2)=NH_2^+$), pyridinium ($C_5H_6N^+$), and mixtures and derivatives thereof. Accordingly compositions wherein the phosphate(s) contains (contain) as nitrogen cations those from the group consisting of ammonium, hydrazinium, iminium, pyridinium, and derivatives and mixtures thereof are preferred.

A nitrogen cation which is particularly preferred in the context of the present invention is the guanidinium ion, which is obtainable by protonating guanidine. Guanidine can be described by the formula I:

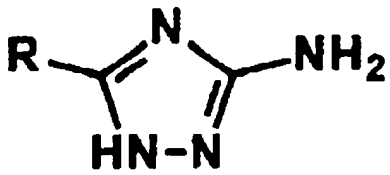


(I)

and is commercialized in the form of colorless, hygroscopic crystals which are readily soluble in alcohol and water, melt at about 50°C, and take up carbon dioxide in the air. Its aqueous solutions are strongly alkaline and form readily crystallizing salts with one equivalent of acid. The cation of the strongly alkaline guanidine, the guanidinium ion $(H_2N)_3C^+$, is resonance stabilized. Compositions which are preferred in the context of the present invention comprise phosphate(s) containing as nitrogen cation the guanidinium ion. Such guanidinium phosphates are, for example $[(H_2N)_3C]H_2PO_4$, $[(H_2N)_3C]_2HPO_4$, $[(H_2N)_3C]_3PO_4$, $[(H_2N)_3C]P_2O_7$, $[(H_2N)_3C]_5P_3O_{10}$, it also being possible for

the hydrogen atoms and/or some of the guanidinium ions to be replaced by alkali metal, especially sodium and/or potassium.

A further nitrogen cation phosphate preferred for use in the context of the present invention possesses as its cation protonated 3-amino-5-alkyl-1,2,4-triazoles. Particular preference is given in this context to the use of the 3-amino-5-alkyl-1,2,4-triazoles and/or their salts of the general formula (II)



(II)

protonation taking place at the amino group and the cation being resonance stabilized. The radical R may be selected from linear and branched alkyl radicals. Preferred radicals R are linear alkyl radicals having 1 to 18 carbon atoms, and so preferred 3-amino-5-alkyl-1,2,4-triazole cations are selected from the following group: 3-amino-5-methyl-1,2,4-triazolium, 3-amino-5-ethyl-1,2,4-triazolium, 3-amino-5-propyl-1,2,4-triazolium, 3-amino-5-butyl-1,2,4-triazolium, 3-amino-5-pentyl-1,2,4-triazolium, 3-amino-5-hexyl-1,2,4-triazolium, 3-amino-5-heptyl-1,2,4-triazolium, 3-amino-5-octyl-1,2,4-triazolium, 3-amino-5-nonyl-1,2,4-triazolium, 3-amino-5-decyl-1,2,4-triazolium, 3-amino-5-undecyl-1,2,4-triazolium, 3-amino-5-dodecyl-1,2,4-triazolium, 3-amino-5-tridecyl-1,2,4-triazolium, 3-amino-5-tetradecyl-1,2,4-triazolium, 3-amino-5-pentadecyl-1,2,4-triazolium, 3-amino-5-hexadecyl-1,2,4-triazolium, 3-amino-5-heptadecyl-1,2,4-triazolium, 3-amino-5-octadecyl-1,2,4-triazolium. Preferred compositions are those wherein the phosphate(s) contains (contain) as nitrogen cation the (3-amino-5-

alkyl-1,2,4-triazol)ium ion, preferred alkyl radicals in the molecule being linear C_{1-18} alkyl radicals, with particular preference being given to hexyl, heptyl, octyl, nonyl and decyl radicals.

The abovementioned cations are a constituent of phosphates. These salts contain phosphate anions, which exist in great diversity. In the context of the present invention, the term "phosphates" denotes the salts of the various phosphoric acids. In the case of the inorganic phosphates, the primary orthophosphates of the general formula $M^{I}H_2PO_4$ and $M^{II}(H_2PO_4)_2$, which are derived from orthophosphoric acid (H_3PO_4), are known; they are all soluble in water and give an acidic reaction. If two hydrogen atoms of the H_3PO_4 are replaced by metal, the secondary orthophosphates are obtained, of the general formula $M^{I}_2HPO_4$ and $M^{II}HPO_4$; of these, only the alkali metal salts dissolve (readily) in water; the solutions given an almost neutral reaction. If all 3 hydrogen atoms of H_3PO_4 are replaced by metal, then tertiary orthophosphates of the general formula $M^{I}_3PO_4$ and $M^{II}_3(PO_4)_2$ are formed; with the exception of the readily soluble, alkaline alkali metal salts, these are virtually insoluble in water, but mostly soluble in strong acids, and do not change when calcined. Derived from the acidic salts of orthophosphoric acid is the extensive group of the condensed phosphates, which are formed by egress of water on heating, and which may be subdivided in turn into metaphosphates (systematic designation: cyclo-polyphosphates) and polyphosphates (systematic designation: catena-polyphosphates).

Compositions which are preferred in the context of the present invention are those comprising as phosphates those from the group consisting of ortho-, pyro-, meta- and polyphosphates, with particular preference being given to the tripolyphosphates.

Combining the comments made above regarding the preferred cations and regarding the preferred phosphate anions, phosphates particularly suitable for the present invention are produced. The present invention therefore further provides compositions for the machine washing of tableware and kitchenware, comprising phosphate(s) and, optionally, further detergent ingredients, which comprise pentaguanidinium triphosphate.

Pentaguanidinium tripolyphosphate, $[(H_2N)_3C]_5P_3O_{10}$, was described earlier above. The machine dishwashing compositions of the invention may be provided in any presentation form, i.e., for example, as powders, granules, extrudates, flakes, beads (pearls), platelets, compact tablets, liquids, or gels. Depending on compounding and the specific profile of requirements, these compositions may contain the pentaguanidinium triphosphate in varying amounts. Preferred compositions contain pentaguanidinium triphosphate in amounts of from 0.1 to 99% by weight, preferably from 1 to 95% by weight, with particular preference from 5 to 90% by weight, and in particular from 10 to 80% by weight, based in each case on the composition.

The present invention further provides compositions for the machine washing of tableware and kitchenware, comprising phosphate(s) and, optionally, further detergent ingredients, which comprise penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate.

The penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphates, $[RC_2N_4H_4]_5P_3O_{10}$, were also described above. When these phosphates are used, it is again possible to realize any presentation form and to vary the penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate content

of the compositions. Preferred compositions contain penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate in amounts of from 0.1 to 99% by weight, preferably from 1 to 95% by weight, with particular preference from 5 to 90% by weight, and in particular from 10 to 80% by weight, based in each case on the composition.

As already mentioned above, certain alkyl radicals are preferred. Particularly preferred compositions are, therefore, those wherein the alkyl radical in the penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphates is selected from the group consisting of hexyl, heptyl, octyl, nonyl, and decyl radicals.

In addition to the phosphates containing nitrogen cations, and further phosphates used optionally, the compositions of the invention for machine dishwashing may comprise further ingredients. From the group of the builders, mention may be made here in particular of silicates and carbonates, and also of the zeolites.

Suitable crystalline, layered sodium silicates possess the general formula $NaMSi_xO_{2x+1}\cdot yH_2O$, where M is sodium or hydrogen, x is a number from 1.9 to 4, y is a number from 0 to 20, and preferred values for x are 2, 3 or 4. Crystalline phyllosilicates of this kind are described, for example, in European Patent Application **EP-A-0 164 514**. Preferred crystalline phyllosilicates of the formula indicated are those in which M is sodium and x adopts the value 2 or 3. In particular, both β- and δ-sodium disilicates $Na_2Si_2O_5\cdot yH_2O$ are preferred, β-sodium disilicate, for example, being obtainable by the process described in International Patent Application **WO-A-91/08171**.

It is also possible to use amorphous sodium silicates having an $Na_2O:SiO_2$ modulus of from 1:2 to 1:3.3, preferably from 1:2 to 1:2.8, and in particular from

1:2 to 1:2.6, which are dissolution-retarded and have secondary washing properties. The retardation of dissolution relative to conventional amorphous sodium silicates may have been brought about in a variety of ways - for example, by surface treatment, compounding, compacting, or overdrying. In the context of this invention, the term "amorphous" also embraces "X-ray-amorphous". This means that in X-ray diffraction experiments the silicates do not yield the sharp X-ray reflections typical of crystalline substances but instead yield at best one or more maxima of the scattered X-radiation, having a width of several degree units of the diffraction angle. However, good builder properties may result, even particularly good builder properties, if the silicate particles in electron diffraction experiments yield vague or even sharp diffraction maxima. The interpretation of this is that the products have microcrystalline regions with a size of from 10 to several hundred nm, values up to max. 50 nm and in particular up to max. 20 nm being preferred. So-called X-ray-amorphous silicates of this kind, which likewise possess retarded dissolution relative to the conventional waterglasses, are described, for example, in German Patent Application **DE-A-44 00 024**. Particular preference is given to compacted amorphous silicates, compounded amorphous silicates, and overdried X-ray-amorphous silicates.

The finely crystalline, synthetic zeolite which can be used, containing bound water, is preferably zeolite A and/or P. A particularly preferred zeolite P is Zeolite MAP® (commercial product from Crosfield). Also suitable, however, are zeolite X and also mixtures of A, X and/or P. A product available commercially and able to be used with preference in the context of the present invention, for example, is a cocrystallizate of zeolite X and zeolite A (approximately 80% by weight zeolite X), which is sold by CONDEA Augusta S.p.A.

under the brand name VEGOBOND AX® and may be described by the formula

$$nNa_2O \cdot (1-n)K_2O \cdot Al_2O_3 \cdot (2-2.5)SiO_2 \cdot (3.5-5.5)H_2O.$$

Suitable zeolites have an average particle size of less than 10 µm (volume distribution; measurement method: Coulter counter) and contain preferably from 18 to 22% by weight, in particular from 20 to 22% by weight, of bound water.

Organic cobuilders which may be used in the machine dishwashing compositions of the invention are, in particular, polycarboxylates/polycarboxylic acids, polymeric polycarboxylates, aspartic acid, polyacetals, dextrins, further organic cobuilders (see below), and phosphonates. These classes of substance are described below.

Organic builder substances which may be used are, for example, the polycarboxylic acids, usable in the form of their sodium salts, the term polycarboxylic acids meaning those carboxylic acids which carry more than one acid function. Examples of these are citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids, amino carboxylic acids, nitrilotriacetic acid (NTA), provided such use is not objectionable on ecological grounds, and also mixtures thereof. Preferred salts are the salts of the polycarboxylic acids such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids, and mixtures thereof.

The acids per se may also be used. In addition to their builder effect, the acids typically also possess the property of an acidifying component and thus also serve to establish a lower and milder pH of laundry detergents or cleaning products. In this context,

mention may be made in particular of citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid, and any desired mixtures thereof.

Also suitable as builders are polymeric polycarboxylates; these are, for example, the alkali metal salts of polyacrylic acid or of polymethacrylic acid, examples being those having a relative molecular mass of from 500 to 70,000 g/mol.

The molecular masses reported for polymeric polycarboxylates, for the purposes of this document, are weight-average molecular masses, M_w, of the respective acid form, determined basically by means of gel permeation chromatography (GPC) using a UV detector. The measurement was made against an external polyacrylic acid standard, which owing to its structural similarity to the polymers under investigation provides realistic molecular weight values. These figures differ markedly from the molecular weight values obtained using polystyrenesulfonic acids as the standard. The molecular masses measured against polystyrenesulfonic acids are generally much higher than the molecular masses reported in this document.

Suitable polymers are, in particular, polyacrylates, which preferably have a molecular mass of from 2000 to 20,000 g/mol. Owing to their superior solubility, preference in this group may be given in turn to the short-chain polyacrylates, which have molecular masses of from 2000 to 10,000 g/mol, and with particular preference from 3000 to 5000 g/mol.

Also suitable are copolymeric polycarboxylates, especially those of acrylic acid with methacrylic acid and of acrylic acid or methacrylic acid with maleic acid. Copolymers which have been found particularly

suitable are those of acrylic acid with maleic acid which contain from 50 to 90% by weight acrylic acid and from 50 to 10% by weight maleic acid. Their relative molecular mass, based on free acids, is generally from 2000 to 70,000 g/mol, preferably from 20,000 to 50,000 g/mol, and in particular from 30,000 to 40,000 g/mol.

The (co)polymeric polycarboxylates can be used either as powders or as aqueous solutions. The (co)polymeric polycarboxylate content of the compositions is preferably from 0.5 to 20% by weight, in particular from 3 to 10% by weight.

In order to improve the solubility in water, the polymers may also contain allylsulfonic acids, such as allyloxybenzenesulfonic acid and methallylsulfonic acid, for example, as monomers.

Particular preference is also given to biodegradable polymers comprising more than two different monomer units, examples being those comprising, as monomers, salts of acrylic acid and of maleic acid, and also vinyl alcohol or vinyl alcohol derivatives, or those comprising, as monomers, salts of acrylic acid and of 2-alkylallylsulfonic acid, and also sugar derivatives.

Further preferred copolymers are those described in German Patent Applications **DE-A-43 03 320** and **DE-A-44 17 734**, whose monomers are preferably acrolein and acrylic acid/acrylic acid salts, and, respectively, acrolein and vinyl acetate.

Similarly, further preferred builder substances that may be mentioned include polymeric amino dicarboxylic acids, their salts or their precursor substances. Particular preference is given to polyaspartic acids and their salts and derivatives, which are disclosed in

German Patent Application **DE-A-195 40 086** to have not only cobuilder properties but also a bleach-stabilizing action.

Further suitable builder substances are polyacetals, which may be obtained by reacting dialdehydes with polyol carboxylic acids having 5 to 7 carbon atoms and at least 3 hydroxyl groups. Preferred polyacetals are obtained from dialdehydes such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyol carboxylic acids such as gluconic acid and/or glucoheptonic acid.

Further suitable organic builder substances are dextrins, examples being oligomers and polymers of carbohydrates, which may be obtained by partial hydrolysis of starches. The hydrolysis can be conducted by customary processes; for example, acid-catalyzed or enzyme-catalyzed processes. The hydrolysis products preferably have average molecular masses in the range from 400 to 500,000 g/mol. Preference is given here to a polysaccharide having a dextrose equivalent (DE) in the range from 0.5 to 40, in particular from 2 to 30, DE being a common measure of the reducing effect of a polysaccharide in comparison to dextrose, which possesses a DE of 100. It is possible to use both maltodextrins having a DE of between 3 and 20 and dried glucose syrups having a DE of between 20 and 37, and also so-called yellow dextrins and white dextrins having higher molecular masses, in the range from 2000 to 30,000 g/mol.

The oxidized derivatives of such dextrins comprise their products of reaction with oxidizing agents which are able to oxidize at least one alcohol function of the saccharide ring to the carboxylic acid function. Oxidized dextrins of this kind, and processes for preparing them, are known, for example, from European

Patent Applications **EP-A-0 232 202, EP-A-0 427 349, EP-A-0 472 042** and **EP-A-0 542 496** and from International Patent Applications **WO 92/18542, WO 93/08251, WO 93/16110, WO 94/28030, WO 95/07303, WO 95/12619** and **WO 95/20608**. Likewise suitable is an oxidized oligosaccharide in accordance with German Patent Application **DE-A-196 00 018**. A product oxidized at C_6 of the saccharide ring may be particularly advantageous.

Oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate, are also further suitable cobuilders. Ethylenediamine N,N'-disuccinate (EDDS) is used preferably in the form of its sodium or magnesium salts. Further preference in this context is given to glycerol disuccinates and glycerol trisuccinates as well. Suitable use amounts in formulations containing zeolite and/or silicate are from 3 to 15% by weight.

Examples of further useful organic cobuilders are acetylated hydroxy carboxylic acids and their salts, which may also be present in lactone form and which contain at least 4 carbon atoms, at least one hydroxyl group, and not more than two acid groups. Such cobuilders are described, for example, in International Patent Application **WO 95/20029**.

A further class of substance having cobuilder properties is represented by the phosphonates. The phosphonates in question are, in particular, hydroxyalkane- and aminoalkanephosphonates. Among the hydroxyalkanephosphonates, 1-hydroxyethane-1,1-diphosphonate (HEDP) is of particular importance as a cobuilder. It is used preferably as the sodium salt, the disodium salt being neutral and the tetrasodium salt giving an alkaline (pH 9-10) reaction. Suitable aminoalkanephosphonates are preferably ethylenediamine-

tetramethylenephosphonate (EDTMP), diethylenetriamine-pentamethylenephosphonate (DTPMP), and their higher homologs. They are used preferably in the form of the neutrally reacting sodium salts, e.g., as the hexasodium salt of EDTMP or as the hepta- and octa-sodium salt of DTPMP. As a builder in this case, preference is given to using HEDP from the class of the phosphonates. Furthermore, the aminoalkanephosphonates possess a pronounced heavy metal binding capacity. Accordingly, and especially if the compositions also contain bleach, it may be preferred to use aminoalkanephosphonates, expecially DTPMP, or to use mixtures of said phosphonates.

Furthermore, all compounds capable of forming complexes with alkaline earth metal ions may be used as cobuilders.

In addition to the builders, important detergent ingredients are, in particular, substances from the group consisting of bleaches, bleach activators, surfactants, enzymes, corrosion inhibitors, dyes and fragrances.

Among the compounds used as bleaches which yield H_2O_2 in water, particular importance is possessed by sodium percarbonate, sodium perborate tetrahydrate and sodium perborate monohydrate. Further bleaches which may be used are, for example, peroxypyrophosphates, citrate perhydrates, and H_2O_2-donating peracidic salts or peracids, such as perbenzoates, peroxophthalates, diperazelaic acid, phthaloiminoper acid or diperdodecanedioic acid. Cleaning products of the invention may also comprise bleaches from the group of organic bleaches. Typical organic bleaches are the diacyl peroxides, such as dibenzoyl peroxide, for example. Further typical organic bleaches are the peroxy acids, particular examples being the alkyl

peroxy acids and the aryl peroxy acids. Preferred representatives are (a) peroxybenzoic acid and its ring-substituted derivatives, such as alkylperoxybenzoic acids, and also peroxy-α-naphthoic acid and magnesium monoperphthalate, (b) aliphatic or substituted aliphatic peroxy acids, such as peroxylauric acid, peroxystearic acid, ε-phthalimidoperoxy caproic acid [phthaloiminoperoxyhexanoic acid (PAP)], o-carboxybenzamidoperoxycaproic acid, N-nonenylamidoperadipic acid and N-nonenylamidopersuccinates, and (c) aliphatic and araliphatic peroxy dicarboxylic acids, such as 1,12-diperoxydecanedicarboxylic acid, 1,9-diperoxyazelaic acid, diperoxysebacic acid, diperoxybrassylic acid, the diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-dioic acid and N,N-terephthaloyldi(6-aminopercaproic acid) may be used.

Bleaches used in the machine dishwashing detergents of the invention may also be substances which release chlorine or bromine. Among suitable chlorine- or bromine-releasing materials, examples include heterocyclic N-bromoamides and N-chloroamides, examples being trichloroisocyanuric acid, tribromoisocyanuric acid, dibromoisocyanuric acid and/or dichloroisocyanuric acid (DICA) and/or salts thereof with cations such as potassium and sodium. Hydantoin compounds, such as 1,3-dichloro-5,5-dimethylhydantoin, are likewise suitable.

The bleaches are used in machine dishwashing compositions usually in amounts of from 1 to 30% by weight, preferably from 2.5 to 20% by weight, and in particular from 5 to 15% by weight, based in each case on the composition. In the context of the present invention preferred compositions comprise one or more bleaches, preferably from the group of the oxygen or halogen bleaches, especially the chlorine bleaches,

with particular preference being given to sodium percarbonate and/or sodium perborate monohydrate, in amounts of from 0.5 to 40% by weight, preferably from 1 to 30% by weight, with particular preference from 2.5 to 25% by weight, and in particular from 5 to 20% by weight, based in each case on the total composition.

Bleach activators, which boost the action of the bleaches, may likewise be a constituent of the detergents of the invention. Known bleach activators are compounds containing one or more N-acyl and/or O-acyl groups, such as substances from the class of the anhydrides, esters, imides and acylated imidazoles or oximes. Examples are tetraacetylethylenediamine TAED, tetraacetylmethylene-diamine TAMD, and tetraacetyl-hexylenediamine TAHD, and also pentaacetylglucose PAG, 1,5-diacetyl-2,2-dioxohexahydro-1,3,5-triazine DADHT, and isatoic anhydride ISA.

Bleach activators which may be used are compounds which under perhydrolysis conditions give rise to aliphatic peroxo carboxylic acids having preferably 1 to 10 carbon atoms, in particular 2 to 4 carbon atoms, and/or substituted or unsubstituted perbenzoic acid. Suitable substances are those which carry O-acyl and/or N-acyl groups of the stated number of carbon atoms, and/or substituted or unsubstituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetylethylenediamine (TAED), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexa-hydro-1,3,5-triazine (DADHT), acylated glycolurils, especially tetraacetylglycoluril (TAGU), N-acyl imides, especially N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, especially n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, especially phthalic anhydride, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate, 2,5-diacetoxy-2,5-dihydro-

furan, N-methylmorpholiniumacetonitrile methyl sulfate (MMA), and the enol esters known from German Patent Applications **DE 196 16 693** and **DE 196 16 767**, and also acetylated sorbitol and mannitol and/or mixtures thereof (SORMAN), acylated sugar derivatives, especially pentaacetylglucose (PAG), pentaacetylfructose, tetraacetylxylose and octaacetyllactose, and acetylated, optionally N-alkylated glucamine and gluconolactone, and/or N-acylated lactams, for example, N-benzoylcaprolactam. Hydrophilically substituted acylacetals and acyllactams are likewise used with preference. Combinations of conventional bleach activators may also be used. The bleach activators are used in machine dishwashing compositions usually in amounts of from 0.1 to 20% by weight, preferably from 0.25 to 15% by weight, and in particular from 1 to 10% by weight, based in each case on the composition.

In addition to the conventional bleach activators, or instead of them, it is also possible to incorporate what are known as bleaching catalysts into the detergents of the invention. These substances are bleach-boosting transition metal salts or transition metal complexes such as, for example, Mn-, Fe-, Co-, Ru- or Mo-salen complexes or -carbonyl complexes. Other bleaching catalysts which can be used include Mn, Fe, Co, Ru, Mo, Ti, V and Cu complexes with N-containing tripod ligands, and also Co-, Fe-, Cu- and Ru-ammine complexes.

Preference is given to the use of bleach activators from the group of polyacylated alkylenediamines, especially tetraacetylethylenediamine (TAED), N-acyl imides, especially N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, especially n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), N-methylmorpholiniumacetonitrile methyl sulfate (MMA), preferably in amounts of up to 10% by weight, in

particular from 0.1% by weight to 8% by weight, more particularly from 2 to 8% by weight, and with particular preference from 2 to 6% by weight, based on the total composition.

Bleach-boosting transition metal complexes, especially those with the central atoms Mn, Fe, Co, Cu, Mo, V, Ti and/or Ru, preferably selected from the group of manganese and/or cobalt salts and/or complexes, with particular preference from cobalt ammine complexes, cobalt acetato complexes, cobalt carbonyl complexes, the chlorides of cobalt or manganese, and manganese sulfate, are used in customary amounts, preferably in an amount of up to 5% by weight, in particular from 0.0025% by weight to 1% by weight, and with particular preference from 0.01% by weight to 0.25% by weight, based in each case on the total composition. In specific cases, however, it is also possible to use a greater amount of bleach activator.

Compositions which are preferred in the context of the present invention comprise one or more substances from the group of the bleach activators, especially from the groups of polyacylated alkylenediamines, especially tetraacetylethylenediamine (TAED), N-acyl imides, especially N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, especially n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), and N-methylmorpholiniumacetonitrile methyl sulfate (MMA), in amounts of from 0.1 to 20% by weight, preferably from 0.5 to 15% by weight, and in particular from 1 to 10% by weight, based in each case on the total composition.

Surfactants used in machine dishwashing compositions are usually only low-foaming nonionic surfactants. Representatives from the groups of the anionic, cationic and amphoteric surfactants, in contrast, are

of relatively little importance. With particular preference, the detergents of the invention for machine dishwashing comprise nonionic surfactants.

In particularly preferred embodiments of the present invention the detergents of the invention comprise nonionic surfactants especially nonionic surfactants from the group of the alkoxylated alcohols. Preferred nonionic surfactants used are alkoxylated, advantageously ethoxylated, especially primary alcohols having preferably 8 to 18 carbon atoms and on average from 1 to 12 mol of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical may be linear or, preferably, methyl-branched in position 2 and/or may contain a mixture of linear and methyl-branched radicals, as are customarily present in oxo alcohol radicals. Particular preference is given, however, to alcohol ethoxylates having linear radicals from alcohols of natural origin having 12 to 18 carbon atoms, e.g., from coconut, palm, tallow fatty or oleyl alcohol, and having on average from 2 to 8 EO per mole of alcohol. The preferred ethoxylated alcohols include, for example, C_{12-14} alcohols having 3 EO or 4 EO, C_{9-11} alcohol having 7 EO, C_{13-15} alcohols having 3 EO, 5 EO, 7 EO or 8 EO, C_{12-18} alcohols having 3 EO, 5 EO or 7 EO, and mixtures of these, such as mixtures of C_{12-14} alcohol having 3 EO and C_{12-18} alcohol having 5 EO. The stated degrees of ethoxylation are statistical means, which for a specific product may be an integer or a fraction. Preferred alcohol ethoxylates have a narrowed homolog distribution (narrow range ethoxylates, NREs). In addition to these nonionic surfactants, fatty alcohols having more than 12 EO may also be used. Examples thereof are tallow fatty alcohol having 14 EO, 25 EO, 30 EO, or 40 EO.

As further nonionic surfactants, furthermore, use may also be made of alkyl glycosides of the general formula

$RO(G)_x$, where R is a primary straight-chain or methyl-branched aliphatic radical, especially an aliphatic radical methyl-branched in position 2, containing 8 to 22, preferably 12 to 18, carbon atoms, and G is the symbol representing a glycose unit having 5 or 6 carbon atoms, preferably glucose. The degree of oligomerization, x, which indicates the distribution of monoglycosides and oligoglycosides, is any desired number between 1 and 10; preferably, x is from 1.2 to 1.4.

A further class of nonionic surfactants used with preference, which are used either as sole nonionic surfactant or in combination with other nonionic surfactants, are alkoxylated, preferably ethoxylated, or ethoxylated and propoxylated, fatty acid alkyl esters, preferably having 1 to 4 carbon atoms in the alkyl chain, especially fatty acid methyl esters, as are described, for example, in Japanese Patent Application **JP 58/217598**, or those prepared preferably by the process described in International Patent Application **WO-A-90/13533**.

Nonionic surfactants of the amine oxide type, examples being N-cocoalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethylamine oxide, and of the fatty acid alkanolamide type, may also be suitable. The amount of these nonionic surfactants is preferably not more than that of the ethoxylated fatty alcohols, in particular not more than half thereof.

Further suitable surfactants are polyhydroxy fatty acid amides of the formula (III),

$$R\text{-}CO\text{-}N(R^1)\text{-}[Z] \qquad \text{(III)}$$

where RCO is an aliphatic acyl radical having 6 to 22 carbon atoms, R^1 is hydrogen or an alkyl or hydroxyalkyl radical having 1 to 4 carbon atoms, and [Z] is a linear or branched polyhydroxyalkyl radical having 3 to 10 carbon atoms and from 3 to 10 hydroxyl groups. The polyhydroxy fatty acid amides are known substances which are customarily obtainable by reductive amination of a reducing sugar with ammonia, an alkylamine or an alkanolamine, and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

The group of the polyhydroxy fatty acid amides also includes compounds of the formula (IV)

$$\begin{array}{l} R^1\text{-}O\text{-}R^2 \\ | \\ R\text{-}CO\text{-}N\text{-}[Z] \end{array} \qquad \text{(IV)}$$

where R is a linear or branched alkyl or alkenyl radical having 7 to 12 carbon atoms, R^1 is a linear, branched or cyclic alkyl radical or an aryl radical having 2 to 8 carbon atoms and R^2 is a linear, branched or cyclic alkyl radical or an aryl radical or an oxyalkyl radical having 1 to 8 carbon atoms, preference being given to C_{1-4} alkyl radicals or phenyl radicals, and [Z] is a linear polyhydroxyalkyl radical whose alkyl chain is substituted by at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated, derivatives of said radical.

[Z] is preferably obtained by reductive amination of a reduced sugar, e.g., glucose, fructose, maltose, lactose, galactose, mannose, or xylose. The N-alkoxy- or N-aryloxy-substituted compounds may then be converted to the desired polyhydroxy fatty acid amides,

for example, in accordance with the teaching of International Patent Application WO-A-95/07331 by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst.

In addition to the straight nonionic surfactants it is of course also possible for other substances, from the group of the ionic surfactants, for example the anionic or cationic surfactants, to be present in the machine dishwashing compositions of the invention.

Compositions which are preferred in the context of the present invention comprise surfactant(s), preferably nonionic surfactant(s), in amounts of from 0.5 to 10% by weight, preferably from 0.75 to 7.5% by weight, and in particular from 1.0 to 5% by weight, based in each case on the total composition.

In order to remove certain types of soiling it is advantageous to add enzymes or enzyme mixtures to cleaning products. Depending on their compounding, the cleaning products of the invention may comprise enzymes, preferably in the form of solid or liquid enzyme preparations. The enzymes for optional use in solid machine dishwashing detergents are preferably commercially customary, solid enzyme preparations.

The enzymes most frequently used in laundry detergents and cleaning products include lipases, cellulases, amylases and proteases. In addition, hemicellulases, peroxidases and pectinases are used in specialty products. In machine dishwashing detergents, proteases, amylases and lipases are of particular importance. Suitable enzymes include in particular those from the classes of the hydrolases such as the proteases, esterases, lipases or lipolytic enzymes, amylases, glycosyl hydrolases, and mixtures of said enzymes. All of these hydrolases contribute to removing stains, such

as proteinaceous, fatty or starchy marks. For bleaching, it is also possible to use oxidoreductases. Especially suitable enzymatic active substances are those obtained from bacterial strains or fungi, such as Bacillus subtilis, Bacillus licheniformis, Streptomyces griseus, Coprinus cinereus and Humicola insolens, and also from genetically modified variants thereof. Preference is given to the use of proteases of the subtilisin type, and especially to proteases obtained from Bacillus lentus. Of particular interest in this context are enzyme mixtures, examples being those of protease and amylase or protease and lipase or lipolytic enzymes, or of protease, amylase and lipase or lipolytic enzymes, or protease, lipase or lipolytic enzymes, but especially protease and/or lipase-containing mixtures or mixtures with lipolytic enzymes. Examples of such lipolytic enzymes are the known cutinases. Peroxidases or oxidases have also proven suitable in some cases. The suitable amylases include, in particular, alpha-amylases, iso-amylases, pullulanases, and pectinases.

The enzymes may be adsorbed on carrier substances or embedded in coating substances in order to protect them against premature decomposition. The proportion of the enzymes, enzyme mixtures or enzyme granules may be, for example, from about 0.1 to 5% by weight, preferably from 0.5 to about 4.5% by weight. Cleaning products which are preferred in the context of the present invention comprise protease and/or amylase.

For use in powder products or tablets, the enzymes are usually prepared in a granulated and encapsulated form and added in that form to the cleaning product. In liquid cleaning products containing water, these granulated and encapsulated enzymes would breakdown, and so in that case the use of liquid enzyme concentrates is generally preferred. Such liquid enzyme

concentrates are based either, homogeneously, on a propylene glycol/water base or, heterogeneously, as a slurry, or are present in a microencapsulated structure. The use of such liquid enzyme preparations is preferred in liquid or gel cleaning products of the invention.

Preferred liquid proteases are, for example, Savinase® L, Durazym® L, Esperase® L, and Everlase® from Novo Nordisk, Optimase® L, Purafect® L, Purafect® OX L, Properase® L from Genencor International, and BLAP® L from Biozym Ges.m.b.H.
Preferred amylases are Termamyl® L, Duramyl® L, and BAN® from Novo Nordisk, Maxamyl® WL and Purafect® HPAm L from Genencor International.
Preferred lipases are Lipolase® L, Lipolase® ultra L and Lipoprime® L from Novo Nordisk and Lipomax® L from Genencor International.

Slurries or microencapsulated liquid products that may be used are, for example, products such as those designated by SL or, respectively, LCC from Novo Nordisk. Said commercial liquid enzyme preparations contain, for example, from 20 to 90% by weight of propylene glycol or of mixtures of propylene glycol and water. Compositions which are preferred in the context of the present invention are those which further comprise enzymes, preferably in the form of liquid and/or solid enzyme preparations, in amounts of from 0.1 to 10% by weight, preferably from 0.5 to 8% by weight, and in particular from 1 to 5% by weight, based in each case on the total composition.

The cleaning products of the invention may include corrosion inhibitors for protecting the ware or the machine, with special importance in the field of machine dishwashing being possessed, in particular, by silver protectants. The known substances of the prior

art may be used. In general it is possible to use, in particular, silver protectants selected from the group consisting of triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles, alkylaminotriazoles, and transition metal salts or transition metal complexes. Particular preference is given to the use of benzotriazole and/or alkylaminotriazole. Frequently encountered in cleaning formulations, furthermore, are agents containing active chlorine, which may significantly reduce corrosion of the silver surface. In chlorine-free cleaners, use is made in particular of oxygen-containing and nitrogen-containing organic redox-active compounds, such as divalent and trivalent phenols, e.g., hydroquinone, pyrocatechol, hydroxyhydroquinone, gallic acid, phloroglucinol, pyrogallol, and derivatives of these classes of compound. Inorganic compounds in the form of salts and complexes, such as salts of the metals Mn, Ti, Zr, Hf, V, Co and Ce, also find frequent application. Preference is given in this context to the transition metal salts selected from the group consisting of manganese and/or cobalt salts and/or complexes, with particular preference cobalt ammine complexes, cobalt acetato complexes, cobalt carbonyl complexes, the chlorides of cobalt or of manganese and manganese sulfate. Similarly, zinc compounds may be used to prevent corrosion on the ware.

Preferred compositions further comprise at least one silver protectant selected from the group consisting of triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles and alkylaminotriazoles, preferably benzotriazole and/or alkylaminotriazole, in amounts of from 0.001 to 1% by weight, preferably from 0.01 to 0.5% by weight, and in particular from 0.05 to 0.25% by weight, based in each case on the total composition.

Dyes and fragrances may be added to the machine dishwashing compositions of the invention in order to enhance the esthetic appeal of the resulting products and to provide the consumer with not only the performance but also a visually and sensorially "typical and unmistakeable" product. As perfume oils and/or fragrances it is possible to use individual odorant compounds, examples being the synthetic products of the ester, ether, aldehyde, ketone, alcohol, and hydrocarbon types. Odorant compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butyl-cyclohexyl acetate, linalyl acetate, dimethylbenzylcarbinyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethyl methylphenylglycinate, allyl cyclohexylpropionate, styrallyl propionate, and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals having 8-18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilial and bourgeonal; the ketones include, for example, the ionones, α-isomethylionone and methyl cedryl ketone; the alcohols include anethole, citronellol, eugenol, geraniol, linalool, phenylethyl alcohol, and terpineol; the hydrocarbons include primarily the terpenes such as limonene and pinene. Preference, however, is given to the use of mixtures of different odorants, which together produce an appealing fragrance note. Such perfume oils may also contain natural odorant mixtures, as obtainable from plant sources, examples being pine oil, citrus oil, jasmine oil, patchouli oil, rose oil or ylang-ylang oil. Likewise suitable are clary sage oil, camomile oil, clove oil, balm oil, mint oil, cinnamon leaf oil, lime blossom oil, juniperberry oil, vetiver oil, olibanum oil, galbanum oil and labdanum oil, and also orange blossom oil, neroliol, orange peel oil, and sandalwood oil.

The fragrances may be incorporated directly into the cleaning products of the invention; alternatively, it may be advantageous to apply the fragrances to carriers.

In order to enhance the esthetic appeal of the compositions of the invention, they (or parts thereof) may be colored with appropriate dyes. Preferred dyes, whose selection presents no difficulty whatsoever to the skilled worker, possess a high level of storage stability and insensitivity to the other ingredients of the compositions and to light and possess no pronounced affinity for the substrates to be treated with the compositions, such as glass, ceramic, or plastic tableware, so as not to stain them.

As already remarked, the cleaning products of the invention may be provided in a very wide variety of forms. In the context of the present invention, as well as powders and granules, cleaning product tablets in particular have proven to be a suitable form. These cleaning product tablets may comprise all of the ingredients described above, with the abovementioned preferred embodiments applying analogously. The details given below in relation to the tablets of the invention have been worded in line with the particularly preferred phosphates, in order to avoid redundancies, but are not limited thereto.

The present invention, accordingly, further provides tablets of compacted, particulate cleaning product, comprising phosphates and also further customary cleaning product ingredients, said tablets containing pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate in amounts of from 0.1 to 99% by weight, preferably from 1 to 95% by weight, with particular preference from 5 to 90% by

weight, and in particular from 10 to 80% by weight, based in each case on the composition.

These tablets may be produced from particulate premixes of appropriate composition by means of conventional tableting technology. The production of the cleaning product tablets of the invention is not restricted to the compression simply of one particulate premix to form a tablet. Rather, a cleaning product tablet may also be designed in such a way that conventional multilayer tablets are produced by preparing two or more premixes which are compressed with one another. In this case, the premix which is introduced first is not precompressed or is only gently precompressed, in order to acquire a smooth top face which extends parallel with the bottom of the tablet, and final compression to form the finished tablet takes place after the second premix has been introduced. In the case of tablets with three or more layers there is a further, optional precompression following the addition of each premix, before the tablet undergoes final compression after the addition of the last premix.

The production of multiphase tablets is of course not tied to a layer construction; rather, it is also possible to produce core/shell tablets, ring-core tablets, or inlay tablets if multiphase tablets are to be produced. As a result of the multiphase nature of the tablets, advantages may be achieved from the division of certain ingredients between the individual phases or layers. For example, preference is given to cleaning product tablets wherein one layer of the tablet comprises one or more bleaches and the other layer comprises one or more enzymes. It is not only this separation of bleaches and enzymes which may bring advantages; in addition, the separation of bleaches and bleach activators for optional use may be advantageous, so that preference is given to cleaning product tablets

of the invention wherein one layer of the tablet comprises one or more bleaches and the other comprises one or more bleach activators. In addition to the separation of ingredients, the amount of an ingredient which is present in both layers may be different. In principle, the multiphase tablets of the invention may comprise said phosphates having nitrogen cations in equal amount in all phases; however, it has proven advantageous if the phosphate content of the phases is different. Cleaning product tablets which are preferred in the context of the present invention are those consisting of two or more phases, preferably layers, the pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate content of the individual phases being different, based in each case on the weight of the phase.

Owing to the increasing technical effort involved, preference is given in practice to tablets having a maximum of two layers; i.e., preferred cleaning product tablets are those which constitute a two-layer tablet. In analogy to the remarks above, the present invention further provides a process for producing laundry detergent and cleaning product tablets by shape-imparting compression of a particulate premix, wherein said premix contains pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate in amounts of from 0.1 to 99% by weight, preferably from 1 to 95% by weight, with particular preference from 5 to 90% by weight, and in particular from 10 to 80% by weight, based in each case on the premix.

In analogy to the remarks relating to the cleaning product tablets of the invention, the use of further ingredients may also be transferred to the process of the invention. In addition to all of the abovementioned ingredients, the cleaning products of the invention in

tablet form may in particular include disintegration aids in order to facilitate the disintegration of highly compacted tablets. Tablet disintegrants, or disintegration accelerators, are understood in accordance with Römpp (9th edition, Volume 6, p. 4440) and Voigt "*Lehrbuch der pharmazeutischen Technologie*" [Text Book of Pharmaceutical Technology] (6th edition, 1987, pp. 182-184) to be auxiliaries which ensure the rapid disintegration of tablets in water or gastric fluid and the release of the drugs in absorbable form.

These substances increase in volume on ingress of water, with on the one hand an increase in the intrinsic volume (swelling) and on the other hand, by way of the release of gases, the possible generation of a pressure which causes the tablets to disintegrate into smaller particles. Examples of established disintegration aids are carbonate/citric acid systems, with the use of other organic acids also being possible. Examples of swelling disintegration aids are synthetic polymers such as polyvinylpyrrolidone (PVP) or natural polymers and/or modified natural substances such as cellulose and starch and their derivatives, alginates, or casein derivatives.

Preferred laundry detergent and cleaning product tablets contain from 0.5 to 10% by weight, preferably from 3 to 7% by weight, and in particular from 4 to 6% by weight, of one or more disintegration aids, based in each case on the tablet weight.

Preferred disintegrants used in the context of the present invention are cellulose-based disintegrants and so preferred laundry detergent and cleaning product tablets comprise a cellulose-based disintegrant of this kind in amounts from 0.5 to 10% by weight, preferably from 3 to 7% by weight, and in particular from 4 to 6% by weight. Pure cellulose has the formal empirical

composition $(C_6H_{10}O_5)_n$ and, considered formally, is a β-1,4-polyacetal of cellobiose, which itself is constructed of two molecules of glucose. Suitable celluloses consist of from about 500 to 5000 glucose units and, accordingly, have average molecular masses of from 50,000 to 500,000. Cellulose-based disintegrants which can be used also include, in the context of the present invention, cellulose derivatives obtainable by polymer-analogous reactions from cellulose. Such chemically modified celluloses include, for example, products of esterifications and etherifications in which hydroxy hydrogen atoms have been substituted. However, celluloses in which the hydroxy groups have been replaced by functional groups not attached by an oxygen atom may also be used as cellulose derivatives. The group of the cellulose derivatives embraces, for example, alkali metal celluloses, carboxymethylcellulose (CMC), cellulose esters and cellulose ethers and aminocelluloses. Said cellulose derivatives are preferably not used alone as cellulose-based disintegrants but instead are used in a mixture with cellulose. The cellulose derivative content of these mixtures is preferably less than 50% by weight, with particular preference less than 20% by weight, based on the cellulose-based disintegrant. The particularly preferred cellulose-based disintegrant used is pure cellulose, free from cellulose derivatives.

The cellulose used as disintegration aid is preferably not used in finely divided form but instead is converted into a coarser form, for example, by granulation or compaction, before being admixed to the premixes intended for compression. Laundry detergent and cleaning product tablets comprising disintegrants in granular or optionally cogranulated form are described in German Patent Applications **DE 197 09 991** (Stefan Herzog) and **DE 197 10 254** (Henkel) and in

International Patent Application WO98/40463 (Henkel). These documents also provide further details on the production of granulated, compacted or cogranulated cellulose disintegrants. The particle sizes of such disintegrants are usually above 200 µm, preferably between 300 and 1600 µm to the extent of at least 90%, and in particular between 400 and 1200 µm to the extent of at least 90%. The abovementioned, relatively coarse disintegration aids based on cellulose, and those described in more detail in the cited documents, are preferred for use as disintegration aids in the context of the present invention and are available commercially, for example, under the designation Arbocel® TF-30-HG from the company Rettenmaier.

As a further cellulose-based disintegrant or as a constituent of this component it is possible to use microcrystalline cellulose. This microcrystalline cellulose is obtained by partial hydrolysis of celluloses under conditions which attack only the amorphous regions (approximately 30% of the total cellulose mass) of the celluloses and break them up completely but leave the crystalline regions (approximately 70%) intact. Subsequent deaggregation of the microfine celluloses resulting from the hydrolysis yields the microcrystalline celluloses, which have primary particle sizes of approximately 5 µm and can be compacted, for example, to granules having an average particle size of 200 µm.

Cleaning product tablets which are preferred in the context of the present invention further comprise a disintegration aid, preferably a cellulose-based disintegration aid, preferably in granular, cogranulated or compacted form, in amounts of from 0.5 to 10% by weight, preferably from 3 to 7% by weight, and in particular from 4 to 6% by weight, based in each case on the tablet weight.

The ingredients of the cleaning product tablets of the invention are combined in pulverulent or pregranulated form to form a premix for compression, which is subsequently compressed. In this case it is of particular advantage if the premix meets certain conditions. In preferred processes the premix possesses, for example, a bulk density of at least 500 g/l, preferably at least 600 g/l, and in particular at least 700 g/l. In preferred processes of the invention, the premix additionally possesses particle sizes of between 100 and 2000 µm, preferably between 200 and 1800 µm, with particular preference between 400 and 1600 µm, and in particular between 600 and 1400 µm.

The other ingredients of the cleaning product tablets of the invention may also be introduced into the process of the invention, reference being made to the above remarks in this regard.

The tablets of the invention are produced first of all by dry-mixing the constituents, some or all of which may have been pregranulated, and subsequently shaping the dry mixture, in particular by compression to tablets, in which context it is possible to have recourse to conventional processes. To produce the tablets of the invention, the premix is compacted in a so-called die between two punches to form a solid compact. This operation, which is referred to below for short as tableting, is divided into four sections: metering, compaction (elastic deformation), plastic deformation, and ejection.

First of all, the premix is introduced into the die, the fill level and thus the weight and form of the resulting tablet being determined by the position of the lower punch and by the form of the compression tool. Even in the case of high tablet throughputs,

constant metering is preferably achieved by volumetric metering of the premix. In the subsequent course of tableting, the upper punch contacts the premix and is lowered further in the direction of the lower punch. In the course of this compaction the particles of the premix are pressed closer to one another, with a continual reduction in the void volume within the filling between the punches. When the upper punch reaches a certain position (and thus when a certain pressure is acting on the premix), plastic deformation begins, in which the particles coalesce and the tablet is formed. Depending on the physical properties of the premix, a portion of the premix particles is also crushed and at even higher pressures there is sintering of the premix. With an increasing compression rate, i.e., high throughputs, the phase of elastic deformation becomes shorter and shorter, with the result that the tablets formed may have larger or smaller voids. In the final step of tableting, the finished tablet is ejected from the die by the lower punch and conveyed away by means of downstream transport means. At this point in time, it is only the weight of the tablet which has been ultimately defined, since the compacts may still change their form and size as a result of physical processes (elastic relaxation, crystallographic effects, cooling, etc).

Tableting takes place in commercially customary tableting presses, which may in principle be equipped with single or double punches. In the latter case, pressure is built up not only using the upper punch; the lower punch as well moves toward the upper punch during the compression operation, while the upper punch presses downward. For small production volumes it is preferred to use eccentric tableting presses, in which the punch or punches is or are attached to an eccentric disk, which in turn is mounted on an axle having a defined speed of rotation. The movement of these

compression punches is comparable with the way in which a customary four-stroke engine works. Compression can take place with one upper and one lower punch, or else a plurality of punches may be attached to one eccentric disk, the number of die bores being increased correspondingly. The throughputs of eccentric presses vary, depending on model, from several hundred up to a maximum of 3000 tablets per hour.

For greater throughputs, the apparatus chosen comprises rotary tableting presses, in which a relatively large number of dies is arranged in a circle on a so-called die table. Depending on the model, the number of dies varies between 6 and 55, larger dies also being obtainable commercially. Each die on the die table is allocated an upper punch and a lower punch, it being possible again for the compressive pressure to be built up actively by the upper punch or lower punch only or else by both punches. The die table and the punches move around a common, vertical axis, and during rotation the punches, by means of raillike cam tracks, are brought into the positions for filling, compaction, plastic deformation, and ejection. At those sites where considerable raising or lowering of the punches is necessary (filling, compaction, ejection), these cam tracks are assisted by additional low-pressure sections, low tension rails, and discharge tracks. The die is filled by way of a rigid supply means, known as the filling shoe, which is connected to a stock vessel for the premix. The compressive pressure on the premix can be adjusted individually for upper punch and lower punch by way of the compression paths, the buildup of pressure taking place by the rolling movement of the punch shaft heads past displaceable pressure rolls.

In order to increase the throughput, rotary presses may also be provided with two filling shoes, in which case only one half-circle need be traveled to produce one

tablet. For the production of two-layer and multilayer tablets, a plurality of filling shoes are arranged in series, and the gently pressed first layer is not ejected before further filling. By means of an appropriate process regime it is possible in this way to produce laminated tablets and inlay tablets as well, having a construction like that of an onion skin, where in the case of the inlay tablets the top face of the core or of the core layers is not covered and therefore remains visible. Rotary tableting presses can also be equipped with single or multiple tools, so that, for example, an outer circle with 50 bores and an inner circle with 35 bores can be used simultaneously for compresssion. The throughputs of modern rotary tableting presses amount to more than a million tablets per hour.

When tableting with rotary presses it has been found advantageous to perform tableting with minimal fluctuations in tablet weight. Fluctuations in tablet hardness can also be reduced in this way. Slight fluctuations in weight can be achieved as follows:

- use of plastic inserts with small thickness tolerances
- low rotor speed
- large filling shoes
- harmonization between the filling shoe wing rotary speed and the speed of the rotor
- filling shoe with constant powder height
- decoupling of filling shoe and powder charge

To reduce caking on the punches, all of the antiadhesion coatings known from the art are available. Polymer coatings, plastic inserts or plastic punches are particularly advantageous. Rotating punches have also been found advantageous, in which case, where possible, upper punch and lower punch should be of rotatable configuration. In the case of rotating

punches, it is generally possible to do without a plastic insert. In this case the punch surfaces should be electropolished.

It has also been found that long compression times are advantageous. These times can be established using pressure rails, a plurality of pressure rolls, or low rotor speeds. Since the fluctuations in tablet hardness are caused by the fluctuations in the compressive forces, systems should be employed which limit the compressive force. In this case it is possible to use elastic punches, pneumatic compensators, or sprung elements in the force path. In addition, the pressure roll may be of sprung design.

Tableting machines suitable in the context of the present invention are obtainable, for example, from the following companies: Apparatebau Holzwarth GbR, Asperg, Wilhelm Fette GmbH, Schwarzenbek, Hofer GmbH, Weil, Horn & Noack Pharmatechnik GmbH, Worms, IMA Verpackungssysteme GmbH, Viersen, KILIAN, Cologne, KOMAGE, Kell am See, KORSCH Pressen AG, Berlin, and Romaco GmbH, Worms. Examples of further suppliers are Dr. Herbert Pete, Vienna (AU), Mapag Maschinenbau AG, Berne (CH), BWI Manesty, Liverpool (GB), I. Holland Ltd., Nottingham (GB), Courtoy N.V., Halle (BE/LU), and Medicopharm, Kamnik (SI). A particularly suitable apparatus is, for example, the hydraulic double-pressure press HPF 630 from LAEIS, D. Tableting tools are obtainable, for example, from the following companies: Adams Tablettierwerkzeuge, Dresden, Wilhelm Fett GmbH, Schwarzenbek, Klaus Hammer, Solingen, Herber & Söhne GmbH, Hamburg, Hofer GmbH, Weil, Horn & Noack, Pharmatechnik GmbH, Worms, Ritter Pharmatechnik GmbH, Hamburg, Romaco GmbH, Worms, and Notter Werkzeugbau, Tamm. Further suppliers are, for example, Senss AG, Reinach (CH) and Medicopharm, Kamnik (SI).

The tablets can be produced in predetermined three-dimensional forms and predetermined sizes. Suitable three-dimensional forms are virtually any practicable designs - i.e., for example, bar, rod or ingot form, cubes, blocks and corresponding three-dimensional elements having planar side faces, and in particular cylindrical designs with a circular or oval cross section. This latter design covers forms ranging from tablets through to compact cylinders having a height-to-diameter ratio of more than 1.

The portioned compacts may in each case be formed as separate, individual elements corresponding to the predetermined dosage of the cleaning products. It is equally possible, however, to design compacts which combine a plurality of such mass units in one compact, with the ease of separation of smaller, portioned units being provided for in particular by means of predetermined breakage points. For the use of cleaning products in machines of the type customary in Europe, it may be judicious to design the portioned compacts as cylindrical or block-shaped tablets, preference being given to a diameter/height ratio in the range from about 0.5:2 to 2:0.5. Commercially customary hydraulic presses, eccentric presses and rotary presses constitute suitable equipment in particular for producing such compacts.

The three-dimensional form of another embodiment of the tablets is adapted in its dimensions to the dispensing cup of commercially customary dishwashers, so that the tablets can be metered without a dosing aid directly into the dispensing cup, where they dissolve during the initial rinse cycle. Alternatively, it is of course readily possible to use the cleaning product tablets by way of a dosing aid.

Another preferred tablet which can be produced has a platelike or barlike structure with, in alternation, long, thick and short, thin segments, so that individual segments can be broken off from this "slab" at the predetermined breakage points, represented by the short, thin segments, and inserted into the machine. This principle of the "slablike" cleaning product tablet may also be realized in other geometric forms, for example, vertical triangles connected to one another lengthwise at only one of their sides.

However, it is also possible for the various components not to be compressed to a homogeneous tablet, but instead to obtain tablets having a plurality of layers, i.e., at least two layers. In this case it is also possible for these different layers to have different dissolution rates. This may result in advantageous performance properties for the tablets. If, for example, there are components present in the tablets which have adverse effects on each other, then it is possible to integrate one component into the quicker-dissolving layer and the other component into a slower-dissolving layer, so that the first component has already reacted when the second passes into solution. The layer structure of the tablets may be realized in stack form, in which case dissolution of the inner layer(s) at the edges of the tablet takes place at a point when the outer layers have not yet fully dissolved; alternatively, the inner layer(s) may also be completely enveloped by the respectively outerlying layer(s), which prevents premature dissolution of constituents of the inner layer(s).

In one further-preferred embodiment of the invention, a tablet consists of at least three layers, i.e., two outer and at least one inner layer, with at least one of the inner layers comprising a peroxy bleach, while in the stack-form tablet the two outer layers, and in

the case of the envelope-form tablet the outermost layers, are free from peroxy bleach. Furthermore, it is also possible to provide spatial separation of peroxy bleach and any bleach activators and/or enzymes present in one tablet.

Similar effects can also be achieved by coating individual constituents of the cleaning product composition intended for compression, or of the tablet as a whole. For this purpose the elements to be coated may be sprayed, for example with aqueous solutions or emulsions, or else a coating may be obtained by the technique of melt coating.

After compression, the cleaning product tablets possess high stability. The fracture strength of cylindrical tablets can be gaged by way of the parameter of diametral fracture stress. This diametral fracture stress can be determined by

$$\sigma = \frac{2P}{\pi D t}$$

where σ represents the diametral fracture stress (DFS) in Pa, P is the force in N which leads to the pressure exerted on the tablet, which pressure causes the fracture of the tablet, D is the tablet diameter in meters, and t is the tablet height.

In the context of the present invention, alongside powders, granules and the cleaning product tablets described above, liquid machine dishwashing compositions have proven to be an appropriate commercial form. These cleaning product liquids or gels may comprise all of the ingredients described above, the preferred embodiments specified above applying analogously. Again, the details below relating to the

liquid machine dishwashing compositions of the invention have been verbally aligned with the particularly preferred phosphates, in order to avoid redundancy, but are not restricted thereto.

The present invention further provides liquid detergent compositions for machine dishwashing, comprising, in addition to further detergent ingredients for optional use,

a) from 10 to 90% by weight of pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate, and
b) from 10 to 90% by weight of one or more nonsurfactant, water-soluble, liquid binders,
c) from 0 to 40% by weight of water.

Pentaguanidinium triphosphate and penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate were described in detail earlier on above. With regard to preferred alkyl radicals and preferred further ingredients, reference may be made to the remarks given above. In the context of the present specification, a "nonsurfactant" binder refers to binders which do not belong to the class of the surfactants. "Water-soluble" binders for the purposes of the present specification are binders which are miscible fully, i.e., without a miscibility gap, with water at room temperature. The term "liquid binder" refers, finally, to the aggregate state of the binder at 25°C and 1013.25 mbar. Substances which melt or soften only at higher temperatures are therefore not suitable for use in the context of the present invention.

In general, the profile of requirements imposed on the binders present in accordance with the invention in the cleaning product compositions is merely that they are liquid at room temperature (and atmospheric pressure), are fully miscible with water, and are not part of the

group of the surfactants. From the large number of binders which may be used, substances from the group consisting of polyethylene glycols and polypropylene glycols, glycerol, glycerol carbonate, ethylene glycol, propylene glycol, and propylene carbonate have proven in particular to be suitable binders. Cleaning product compositions comprising, as nonsurfactant, water-soluble, liquid binders, one or more substances from the group consisting of polyethylene glycols and polypropylene glycols, glycerol, glycerol carbonate, ethylene glycol, propylene glycol, and propylene carbonate are preferred in the context of the present invention.

Polyethylene glycols (abbreviation PEGs) which can be used in accordance with the invention are polymers of ethylene glycol which satisfy the general formula V

$$H\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}OH \qquad (V)$$

in which n is able to adopt values between 1 (ethylene glycol, see below) and approximately 16. Critical in assessing whether a polyethylene glycol may be used in accordance with the invention is the aggregate state of the PEG at room temperature; i.e., the solidification point of the PEG must be below 25°C. For polyethylene glycols there exist various nomenclatures, which can lead to confusion. It is common in the art to state the average relative molecular weight after the letters "PEG", so that "PEG 200" characterizes a polyethylene glycol having a relative molecular mass of from about 190 to about 210. In accordance with this nomenclature, the technically customary polyethylene glycols PEG 200, PEG 300, PEG 400, and PEG 600 may be used in the context of the present invention.

For cosmetic ingredients a different nomenclature is used, where the abbreviation PEG is provided with a

hyphen and the hyphen is followed directly by a number which corresponds to the number n in the abovementioned formula V. According to this nomenclature (known as the INCI nomenclature, CTFA International Cosmetic Ingredient Dictionary and Handbook, 5th Edition, The Cosmetic, Toiletry and Fragrance Association, Washington, 1997), for example, PEG-4, PEG-6, PEG-8, PEG-9, PEG-10, PEG-12, PEG-14, and PEG-16 may be used in accordance with the invention.

Polyethylene glycols are available commercially, for example, under the trade names Carbowax® PEG 200 (Union Carbide), Emkapol® 200 (ICI Americas), Lipoxol® 200 MED (HÜLS America), Polyglycol® E-200 (Dow Chemical), Alkapol® PEG 300 (Rhone-Poulenc), Lutrol® E300 (BASF), and the corresponding trade names with higher numbers.

In the context of the present invention, particular preference is given to the use of PEG 400, which may if desired be mixed with others of the binders mentioned above and below. Preferred compositions have a PEG 400 content which may be from 0 to 40% by weight, preferably from 5 to 30% by weight, and in particular from 10 to 20% by weight.

Polypropylene glycols (abbreviation PPGs) which may be used in accordance with the invention are polymers of propylene glycol which satisfy the general formula VI

$$H\text{-}(O\text{-}CH(CH_3)\text{-}CH_2)_n\text{-}OH \qquad (VI)$$

in which n may adopt values of between 1 (propylene glycol, see below) and approximately 12. Industrially significant in this case are, in particular, di-, tri- and tetrapropylene glycol, i.e., the representatives where n = 2, 3 and 4 in formula VI.

Glycerol is a colorless, clear, viscous, odorless, hygroscopic liquid which has a sweet taste and a density of 1.261 and solidifies at 18.2°C. Glycerol was originally only a byproduct of fat saponification, but is nowadays synthesized industrially in large quantities. The majority of industrial processes start from propene, which is processed to glycerol via the intermediate stages of allyl chloride and epichlorohydrin. Another industrial process is the hydroxylation of allyl alcohol with hydrogen peroxide over a WO_3 catalyst, which passes via the stage of glycide.

In the context of the present invention, glycerol is a binder whose use is particularly preferred. The glycerol content of preferred aqueous cleaning product compositions is from 10 to 40% by weight, preferably from 15 to 35% by weight, and in particular from 20 to 30% by weight, based in each case on the composition.

Glycerol carbonate is obtainable by transesterifying ethylene carbonate or dimethyl carbonate with glycerol, the byproducts produced being ethylene glycol or methanol, respectively. A further synthesis route starts from glycidol (2,3-epoxy-1-propanol), which is reacted with CO_2 under superatmospheric pressure in the presence of catalysts to form glycerol carbonate. Glycerol carbonate is a clear, mobile liquid having a density of 1.398 g cm^{-3} which boils at 125-130°C (0.15 mbar).

Ethylene glycol (1,2-ethanediol, "glycol") is a colorless, viscous, highly hygroscopic liquid with a sweet taste which is miscible with water, alcohols, and acetone and has a density of 1.113 g cm^{-3}. The solidification point of ethylene glycol is -11.5°C; the liquid boils at 198°C. Industrially, ethylene glycol is

obtained from ethylene oxide by heating with water under superatmospheric pressure. Promising preparation processes may be based on the acetoxylation of ethylene and subsequent hydrolysis, or on synthesis gas reactions.

Propylene glycol exists in two isomeric forms, the 1,3-propanediol and the 1,2-propanediol. 1,3-Propanediol (trimethylene glycol) is a neutral, colorless and odorless liquid with a sweet taste and a density of 1.0597 g cm^{-3} which solidifies at -32°C and boils at 214°C. 1,3-Propanediol is prepared starting from acrolein and water with subsequent catalytic hydrogenation.

Far more important industrially is 1,2-propanediol (propylene glycol), which is an oily, colorless, virtually odorless liquid of density 1.0381 g cm^{-3} which solidifies at -60°C and boils at 188°C. 1,2-Propanediol is prepared from propylene oxide by hydrogen addition. In the context of the present invention, 1,2-propanediol is likewise a binder whose use is preferred. In particular, mixtures of 1,2-propanediol and PEG or of 1,2-propanediol and glycerol, or mixtures of 1,2-propanediol and PEG and glycerol, are preferred binder mixtures in the context of the present invention.

Propylene carbonate is a water-white mobile liquid having a density of 1.2057 g cm^{-3}, a melting point of -49°C, and a boiling point of 242°C. Propylene carbonate is also accessible industrially by reacting propylene oxide and CO_2 at 200°C and 80 bar.

A particularly preferred binder in the context of the present invention is glycerol. Cleaning product compositions whose nonsurfactant, water-soluble, liquid binder comprises glycerol in amounts of from 10 to 80%

by weight, preferably from 15 to 70% by weight, and in particular from 20 to 50% by weight, based in each case on the composition, are preferred in the context of the present invention.

The liquid cleaning product compositions of the invention may comprise water in amounts of up to 40% by weight. Depending on the nature and amount of the other ingredients, this water content may lie within the upper region or within the lower region of said limits. If, for example, bleaches are present in the liquid cleaning products, then the water content chosen is preferably low for reasons of storage stability. Where large quantities of solids are to be suspended stably in respect of settling, it is often desirable to add thickeners, which in turn require a certain amount of water in order to develop their action. A particular advantage of the present invention is that relatively viscous cleaning products can be formulated even without adding water, since the nitrogen cation phosphates used in accordance with the invention produce thickenable systems in nonaqueous solvents or binders even without traces of water. The present invention additionally provides, therefore, liquid nonaqueous cleaning product compositions comprising, in addition to further, optional cleaning product ingredients,

a) from 20 to 50% by weight of pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate,
b) from 1 to 50% by weight of glycerol,
c) from 0 to 40% by weight of a polyethylene glycol which is liquid at room temperature, and
d) from 0 to 20% by weight of 1,2-propanediol
e) ≤ 2% by weight of free water.

The term "free water" refers to the water content of the compositions that is not bound in the form of water

of hydration and/or water of constitution, i.e., only the water which is present in the compositions as a constituent of the liquid matrix. Said content in accordance with the invention is 2% by weight or less, preferably less than 1.5% by weight, with particular preference less than 1% by weight, and in particular even less than 0.5% by weight, based in each case on the composition. Accordingly, preference is given to cleaning product compositions having a corresponding free water content. Accordingly, liquid may be present essentially only in chemically and/or physically bound form or as a constituent of the solid raw materials or compounds, but not as a liquid, solution or dispersion, in the compositions of the invention. Advantageously, the compositions of the invention have an overall water content of not more than 15% by weight, this water thus being present not in liquid, free form but instead in chemically and/or physically bound form; in particular it is preferred that the amount of water not bound to carbonates and/or to silicates in the compositions of the invention is not more than 10% by weight and in particular not more than 7% by weight. For preparing the compositions of the invention it is possible to use liquids containing water provided that the free water content is held below the stated limit by the addition of an "internal siccative", for example, a hydratable substance in nonhydrated form.

Especially with regard to the performance of the liquid cleaning products of the invention and their physical stability (settling behavior) and chemical stability (bleach decomposition), products are provided which combine high performance with high storage and transport stability. Thus the incorporation of bleaches and bleach activators, where desired, is readily possible, and good cleaning performance is achieved even without the use of high levels of surfactant. The invention's preferred liquid matrix comprising glycerol

and, optionally, room-temperature-liquid polyethylene glycols, which may optionally be supplemented further by diols, 1,2-propanediol being particularly suitable, yields excellent results in this context.

In addition to the ingredients described above, the liquid cleaning product compositions of the invention may comprise viscosity regulators and/or thickeners in order to establish a relatively high viscosity if desired. In this case it is possible to use all known thickeners, i.e., those based on natural or synthetic polymers.

Polymers originating from nature which may be used as thickeners are, for example, agar-agar, carrageenan, tragacanth, gum arabic, alginates, pectins, polyoses, guar gum, carob gum, starch, dextrins, gelatin, and casein. Modified natural substances come in particular from the group of the modified starches and celluloses; examples that may be mentioned here include carboxymethylcellulose and other cellulose ethers, hydroxyethylcellulose and hydroxypropylcellulose, and also bean flour ethers.

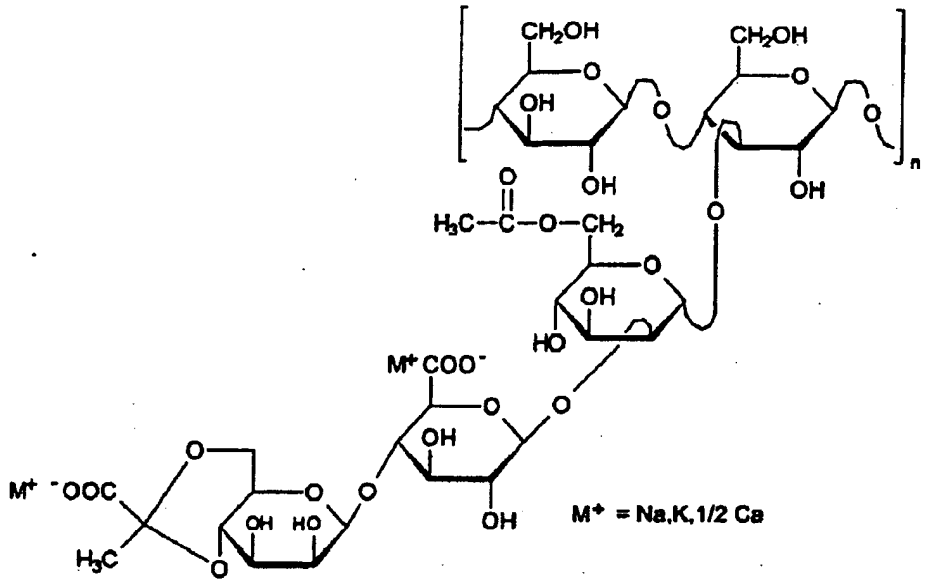
A large group of thickeners which find broad application in a very wide variety of fields of use are the all-synthetic polymers such as polyacrylic and polymethacrylic compounds, vinylpolymers, polycarboxylic acids, polyethers, polyimines, polyamides, and polyurethanes.

Thickeners from said classes of substance are widely available commercially and are obtainable, for example, under the trade names Acusol®-820 (methacrylic acid stearyl alcohol-20 EO) ester-acrylic acid copolymer, 30% in water, Rohm & Haas), Dapral®-GT-282-S (alkyl polyglycol ether, Akzo), Deuterol®-polymer-11 (dicarboxylic acid copolymer, Schöner GmbH), Deuteron®-XG (anionic heteropolysaccharide based on

β-D-glucose, D-mannose, D-glucuronic acid, Schöner GmbH), Deuteron®-XN (nonionic polysaccharide, Schöner GmbH), Dicrylan®-Thickener-O (ethylene oxide adduct, 50% in water/isopropanol, Pfersee Chemie), EMA®-81 and EMA®-91 (ethylene-maleic anhydride copolymer, Monsanto), Thickener QR-1001 (polyurethane emulsion, 19-21% in water/diglycol ether, Rohm & Haas), Mirox®-AM (anionic acrylic acid-acrylate copolymer dispersion, 25% in water, Stockhausen), SER-AD-FX-1100 (hydrophobic urethane polymer, Servo Delden), Shellflo®-S (high molecular mass polysaccharide, stabilized with formaldehyde, Shell), and Shellflo®-XA (xanthan biopolymer, stabilized with formaldehyde, Shell).

A polymeric thickener whose use is preferred is xanthan, a microbial anionic heteropolysaccharide which is produced by Xanthomonas campestris and certain other species under aerobic conditions and has a molecular mass of from 2 to 15 million daltons. Xanthan is formed from a chain comprising β-1,4-linked glucose (cellulose) with side chains. The structure of the subgroups consists of glucose, mannose, glucuronic acid, acetate, and pyruvate, the number of pyruvate units determining the viscosity of the xanthan.

Xanthan may be described by the following formula:



Basic unit of xanthan

Thickeners whose use is likewise preferred in the context of the present invention are polyurethanes or modified polyacrylates, which may be used, for example, in amounts of from 0.1 to 5% by weight, based on the total composition.

Polyurethanes (PUs) are prepared by polyaddition from divalent and higher polyvalent alcohols and isocyanates and may be described by the general formula VII

$$[\text{-O-}R^1\text{-O-C(=O)-NH-}R^2\text{-NH-C(=O)-}]_n \qquad \text{VII,}$$

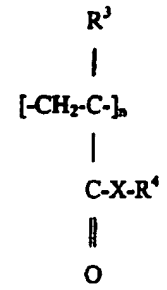
where R^1 is a low molecular mass or polymeric diol radical, R^2 is an aliphatic or aromatic group, and n is a natural number. R^1 is preferably a linear or branched C_{2-12} alk(en)yl group, but may also be a radical of a higher polyhydric alcohol, whereby crosslinked polyurethanes are formed which differ from the formula

VII indicated above in that further -O-CO-NH groups are attached to the radical R^1.

Industrially important PUs are prepared from polyester diols and/or polyether diols and, for example, from 2,4- and/or 2,6-toluene diisocyanate (TDI, $R^2 = C_6H_3-CH_3$), 4,4'-methylenedi(phenylisocyanate) (MDI, $R^2 = C_6H_4-CH_2-C_6H_4$) or hexamethylene diisocyanate [HMDI, $R^2 = (CH_2)_6$].

Commercial thickeners based on polyurethane are obtainable, for example, under the names Acrysol® PM 12 V (mixture of 3-5% modified starch and 14-16% PU resin in water, Rohm & Haas), Borchigel® L75-N (nonionic PU dispersion, 50% in water, Borchers), Coatex® BR-100-P (PU dispersion, 50% in water/butyl glycol, Dimed), Nopco® DSX-1514 (PU dispersion, 40% in water/butyl triglycol, Henkel-Nopco), thickener QR 1001 (20% PU emulsion in water/diglycol ether, Rohm & Haas), and Rilanit® VPW-3116 (PU dispersion, 43% in water, Henkel).

Modified polyacrylates which may be used in the context of the present invention are derived, for example, from acrylic acid or methacrylic acid and may be described by the general formula VIII

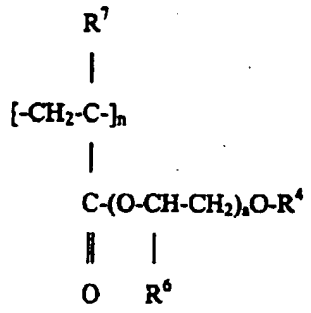


VIII,

where R^3 is H or a branched or unbranched C_{1-4} alk(en)yl radical, X is N-R^5 or O, R^4 is an optionally alkoxylated branched or unbranched, optionally substituted C_{8-22} alk(en)yl radical, R^5 is H or R^4, and n is a natural number. In general, modified polyacrylates of this kind

are esters or amides of acrylic acid or of an α-substituted acrylic acid. Preferred among these polymers are those in which R^3 is H or a methyl group. In the case of the polyacrylamides (X = N-R^5), both singly (R^5 = H) and doubly (R^5 = R^4) N-substituted amide structures are possible, it being possible for the two hydrocarbon radicals attached to the nitrogen atom to be selected, independently of one another, from optionally alkoxylated branched or unbranched C_{8-22} alk(en)yl radicals. Among the polyacrylic esters (X = O), preference is given to those in which the alcohol has been obtained from natural synthetic fats or oils and is additionally alkoxylated, preferably ethoxylated. Preferred degrees of alkoxylation are between 2 and 30, with particular preference being given to degrees of alkoxylation of between 10 and 15. Since the polymers that may be used comprise industrial compounds, the designation of the radicals attached to X represents an average which may vary in terms of chain length and/or degree of alkoxylation in each individual case. The formula VIII indicates merely formulae of idealized homopolymers. In the context of the present invention, however, it is also possible to use copolymers in which the proportion of monomer units which satisfy the formula VIII is at least 30% by weight. For example, it is also possible to use copolymers of modified polyacrylates and acrylic acid, and/or salts thereof, which still possess acidic hydrogen atoms or basic $-COO^-$ groups.

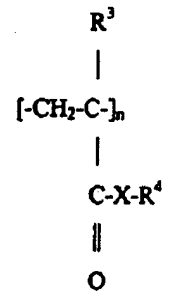
Modified polyacrylates preferred for use in the context of the present invention are polyacrylate-polymethacrylate copolymers which satisfy the formula VIIIa



VIIIa,

where R^4 is a preferably unbranched, saturated or unsaturated C_{8-22} alk(en)yl radical, R^5 and R^7 independently of one another are H or CH_3, the degree of polymerization n is a natural number and the degree of alkoxylation a is a natural number between 2 and 30, preferably between 10 and 20. R^4 is preferably a fatty alcohol residue obtained from natural or synthetic sources, the fatty alcohol in turn being preferably ethoxylated (R^6 = H).
Products of the formula VIIIa are commercially available, for example, under the name Acusol® 820 (Rohm & Haas) in the form of 30% by weight dispersions in water. In that commercial product, R^4 is a stearyl radical, R^6 is a hydrogen atom, R^7 is H or CH_3, and the degree of ethoxylation a is 20.

Liquid cleaning product compositions which are preferred in the context of the present invention are those which further comprise from 0.1 to 5% by weight, preferably from 0.2 to 4% by weight, with particular preference from 0.3 to 3% by weight, and in particular from 0.5 to 1.5% by weight, of a polymeric thickener, preferably from the group of the polyurethanes or modified polyacrylates, with particular preference being given to thickeners of the formula VIII



VIII,

where R^3 is H or a branched or unbranched C_{1-4} alk(en)yl radical, X is N-R^5 or O, R^4 is an optionally alkoxylated branched or unbranched, optionally substituted C_{8-22} alk(en)yl radical, R^5 is H or R^4, and n is a natural number.

The viscosity of the compositions of the invention may be measured with customary standard methods (for example, Brookfield viscometer LVT-II at 20 rpm and 20°C, spindle 3) and is preferably within the range from 500 to 5000 mPas. Preferred cleaning product compositions have viscosities of from 1000 to 4000 mPas, particular preference being given to values of from 1300 to 3000 mPas.
The pH of the undiluted products of the invention is preferably within a range from 6 to 11, with particular preference between 7 and 10, and in particular between 7.5 and 9.

The present invention additionally provides for the use of phosphates with nitrogen cations in machine dishwashing detergents.

In accordance with a preferred embodiment, particular preference is given to the use of phosphates containing exclusively nitrogen cations in machine dishwashing detergents.

Particularly preferred phosphates having nitrogen cations have been described in connection with the

cleaning product tablets and cleaning products of the invention in liquid form. The use of pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate in detergents for machine dishwashing is also provided for by the present invention.

Embodiments of the Invention are described by reference to the following specific examples which are not to be construed as limiting.

Examples:

I. Synthesis of pentaguanidinium triphosphate and penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate

a) Purification of sodium triphosphate

Sodium triphosphate hexahydrate was precipitated from a concentrated aqueous sodium triphosphate solution by adding ethanol (volume ratio ethanol:water = 1:3). The product filtered off with suction was washed with an ethanol/water mixture (volume ratio ethanol:water = 1:1) and dried.

b) Preparation of pentaguanidinium triphosphate:

A solution of 34% by weight of guanidine hydrochloride, 51% by weight of water and 15% by weight of sodium triphosphate hexahydrate purified as per a) was heated to 55°C. Following filtration to remove undissolved constituents, formamide was added dropwise through the dropping funnel containing the residue into the filtrate until the volume ratio water:formamide was 1:7. The precipitate formed was filtered off with suction and washed twice each with formamide and ethanol. Drying gave the crude product in a yield of

73%, based on sodium triphosphate hexahydrate, which was purified. This was done by adding formamide dropwise to a solution of 31% by weight of pentaguanidinium triphosphate and 6% by weight of guanidine hydrochloride in 63% by weight of water until the volume ratio water:formamide was 1:1. The resulting precipitate was filtered off with suction, washed twice each with formamide and ethanol, and dried.

c) Preparation of penta[(3-amino-5-heptyl-1,2,4-triazol)ium] triphosphate:

A solution of 4.5 g of sodium triphosphate hexahydrate purified as per a) in 30 ml of water was added to 49.2 g (0.11 mol) of a 50% strength (3-amino-5-heptyl-1,2,4-triazol)ium hydrochloride solution. The resulting precipitate was filtered off with suction and stirred into 20 ml of n-hexane. The solution was concentrated on a rotary evaporator and the product was dried. Further product was obtained from the mother liquor by adding formamide.

II. Stability of pentaguanidinium triphosphate:

2.5 mmol each of pentaguanidinium triphosphate and pentasodium triphosphate were dissolved in 25 ml of water each time and stored at a temperature of 30°C for a period of 100 hours. The products were subsequently analyzed by ion chromatography. The results are listed in Table 1.

Tab. 1: Hydrolytic stability of the triphosphate salts

Sample 1: $Na_5P_3O_{10}*6H_2O$	**Sample 2: $[C(NH_3)_3]_5P_3O_{10}$**
95.1% $P_3O_{10}^{5-}$	99.1% $P_3O_{10}^{5-}$
4.7% $P_2O_7^{4-}$	0.6% $P_2O_7^{4-}$
0.2% PO_4^{3-}	0.3% PO_4^{3-}

As the analysis shows, after 100 hours in aqueous solution, more than 99% of the pentaguanidinium triphosphate is still present in undecomposed form, and it is thus markedly more stable to hydrolysis than is the pentasodium triphosphate.

III. Cleaning products containing pentaguanidinium triphosphate and their cleaning performance:

The liquid constituents were mixed and the finely ground solids added to prepare the inventive formulation E and the Comparative Example V, whose composition is indicated in Table 2:

Table 2: Nonaqueous dishwasher detergent (% by weight)

	E	V
Pentaguanidinium triphosphate	32.4	-
Sodium triphosphate	-	32.4
Glycerol	39.3	39.3
Perfume	0.7	0.7
Thickener*	0.1	0.1
Sodium carbonate, anhydrous	3.0	3.0
Crystalline δ-sodium disilicate**	6.0	6.0
Sodium percarbonate	10.0	10.0
Tetraacetylethylenediamine	4.0	4.0
Disodium hydroxyethane-1,1-diphosphonate	0.6	0.6
Benzotriazole	0.3	0.3
Dye	0.1	0.1
Amylase preparation***	2.0	2.0
Protease preparation****	1.5	1.5

* Carbopol® ETD 2691 (Goodrich)
** SKS-6® (Clariant)
*** Duramyl® 60 T (Biozym)
**** BLAP® 200 S (Biozym)

The compositions E and V were tested in a customary domestic dishwasher (Miele G 590 with universal

program) under the following washing conditions: 55°C/16°d [German] water hardness measured in the main rinse cycle (i.e., "hard conditions").

The dose was in each case 25 g. Table 3 shows the results of evaluation by an expert panel using the following evaluation scheme: visual evaluation in the case of tea, milk, baked-on meat, and egg/milk by comparison with a picture catalog. The removal of starch is measured by gravimetric determination of the removal of the soiling. Evaluation scheme: rating 0 for ware with original soiling, rating 10 for absolutely clean ware.

Table 2: Cleaning performance

Soil	**E**	**V**
Tea	5.3	5.7
Milk	6.7	7.3
Minced meat in glass dishes	5.5	6.3
Minced meat on porcelain	6.0	6.5
Egg/milk	10.0	10.0
Starch	10.0	10.0

As evident from Table 3, the liquid cleaning product compositions of the invention attain the performance level of comparable compositions containing alkali metal phosphates. At the same time, the compositions of the invention possess a much higher storage stability.

CLAIMS

1. A composition for the machine washing of tableware and kitchenware, comprising phosphate(s) and, optionally, further detergent ingredients, wherein at least one of the phosphates present in said composition contains nitrogen cations.

2. The composition as claimed in claim 1, wherein at least one of the phosphates present in said composition contains exclusively nitrogen cations.

3. The composition as claimed in either of claims 1 and 2, wherein all of the phosphates present in said composition contain nitrogen cations.

4. The composition as claimed in any of claims 1 to 3, wherein all of the phosphates present in said composition contain exclusively nitrogen cations.

5. The composition as claimed in any of claims 1 to 4, wherein the phosphate(s) contains (contain) as nitrogen cations those from the group consisting of ammonium, hydrazinium, iminium, pyridinium and derivatives and mixtures thereof.

6. The composition as claimed in any of claims 1 to 4, wherein the phosphate(s) contains (contain) as nitrogen cation the guanidinium ion.

7. The composition as claimed in any of claims 1 to 4, wherein the phosphate(s) contains (contain) as nitrogen cation, the (3-amino-5-alkyl-1,2,4-triazol)ium ion.

8. The composition as claimed in claim 7, wherein alkyl radicals in the nitrogen cation are linear C_{1-18} alkyl radicals.

9. The composition as claimed in claim 8, wherein the alkyl radical is selected from the group consisting of hexyl, heptyl, octyl, nonyl and decyl radicals.

10. The composition as claimed in any one of claims 1 to 9, which comprises as phosphates those from the group consisting of ortho-, pyro-, meta- and polyphosphates.

11. The composition as claimed in claim 10,wherein the polyphosphate is tripolyphosphate.

12. A composition for the machine washing of tableware and kitchenware, comprising phosphate(s) and, optionally, further detergent ingredients, which comprises pentaguanidinium triphosphate.

13. The composition as claimed in claim 12, which contains pentaguanidinium triphosphate in amounts of from 0.1 to 99% by weight based on the composition.

14. The composition as claimed in claim 13, wherein the pentaguanidinium triphosphate is present in amounts of from 1 to 95% by weight.

15. The composition as claimed in claim 14, wherein the pentaguanidinium triphosphate is present in amounts of from 5 to 90% by weight.

16. The composition as claimed in claim 15, wherein the pentaguanidinium triphosphate is present in amounts of from 10 to 80% by weight.

17. A composition for the machine washing of tableware and kitchenware, comprising phosphate(s) and, optionally, further detergent ingredients, which comprises penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate.

18. The composition as claimed in claim 17, which contains penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate in amounts of from 0.1 to 99% by weight based on the composition.

19. The composition as claimed in claim 18, wherein said triphosphate is present in amounts from 1 to 95% by weight.

20. The composition as claimed in claim 19, wherein said triphosphate is present in amounts from 5 to 90% by weight.

21. The composition as claimed in claim 20, wherein said triphosphate is present in amounts from 10 to 80% by weight.

22. The composition as claimed in any one of claims 17 to 21, wherein the alkyl radical in the penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphates is selected from the group consisting of hexyl, heptyl, octyl, nonyl, and decyl radicals.

23. The composition as claimed in any of claims 1 to 22, further comprising one or more bleaches.

24. The composition as claimed in claim 23, wherein the bleaches are selected from the group consisting of the oxygen or halogen bleaches.

25. The composition as claimed in claim 24, wherein the halogen bleach is a chlorine bleach.

26. The composition as claimed in claim 23, wherein said bleaches are sodium percarbonate and/or sodium perborate monohydrate.

27. The composition as claimed in any one of claims 23 to 26, wherein said bleaches are present in amounts of from 0.5 to 40% by weight based on the total composition.

28. The composition as claimed in claim 27, wherein said bleaches are present in amounts of from 1 to 30% by weight.

29. The composition as claimed in claim 28, wherein said bleaches are present in amounts of from 2.5 to 25% by weight.

30. The composition as claimed in claim 29, wherein said bleaches are present in amounts of from 5 to 20% by weight.

31. The composition as claimed in any of claims 1 to 30, further comprising one or more substances from the group of bleach activators.

32. The composition as claimed in claim 31, wherein said bleach activators are selected from the group consisting of polyacylated alkylenediamines, N-acyl imides and acylated phenolsulfonates.

33. The composition as claimed in claim 32, wherein said alkylenediamine is tetraacetylethylenediamine (TAED).

34. The composition as claimed in claim 32, wherein said N-acyl imide is N-nonanoylsuccinimide (NOSI).

35. The composition as claimed in claim 32, wherein said acylated phenolsulfonate is selected from n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS) and N-methylmorpholiniumacetonitrile methyl sulfate (MMA).

36. The composition as claimed in any one of claims 32 to 35, wherein said bleach activators are present in amounts of from 0.1 to 20% by weight based on the total composition.

37. The composition as claimed in claim 36, wherein said bleach activators are present in amounts of from 0.5 to 15% by weight.

38. The composition as claimed in claim 37, wherein said bleach activators are present in amounts of from 1 to 10% by weight.

39. The composition as claimed in any one of claims 1 to 38, further comprising surfactant(s).

40. The composition as claimed in claim 39, wherein said surfactant(s) are nonionic surfactant(s).

41. The composition as claimed in either of claims 39 or 40, wherein said surfactants are present in amounts of from 0.5 to 10% by weight based on the total composition.

42. The composition as claimed in claim 41, wherein said surfactants are present in amounts of from 0.75 to 7.5% by weight.

43. The composition as claimed in claim 42, wherein said surfactants are present in amounts of from 1.0 to 5% by weight.

44. The composition as claimed in any one of claims 1 to 43, further comprising enzymes.

45. The composition as claimed in claim 44, wherein said enzymes are in the form of liquid and/or solid enzyme preparations.

46. The composition as claimed in either of claims 44 or 45, wherein said enzymes are present in amounts of from 0.1 to 10% by weight based on the total composition.

47. The composition as claimed in claim 46, wherein said enzymes are present in amounts of from 0.5 to 8% by weight.

48. The composition as claimed in claim 47, wherein said enzymes are present in amounts of from 1 to 5% by weight.

49. The composition as claimed in any of claims 1 to 48, further comprising at least one silver protectant selected from the group consisting of triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles, and alkylaminotriazoles.

50. The composition as claimed in claim 49, wherein said silver protectant is benzotriazole and/or alkylaminotriazole.

51. The composition as claimed in either of claims 49 to 50, wherein said silver protectant is present in amounts of from 0.001 to 1% by weight based on the total composition.

52. The composition as claimed in claim 51, wherein said silver protectant is present in amounts of from 0.01 to 0.5% by weight.

53. The composition as claimed in claim 52, wherein said silver protectant is present in amounts of from 0.05 to 0.25% by weight.

54. A tablet of compacted, particulate cleaning product, comprising phosphates and also further customary cleaning product ingredients, which contains pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate in amounts of from 0.1 to 99% by weight based on the total composition.

55. The tablet as claimed in claim 54, containing from 1 to 95% by weight of said triphosphates.

56. The tablet as claimed in claim 55, containing from 5 to 90% by weight of said triphosphates.

57. The tablet as claimed in claim 56, containing from 10 to 80% by weight of said triphosphates.

58. The tablet as claimed in any one of claims 54 to 57, which consists of two or more phases, preferably layers, the pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate content of the individual phases being different, based in each case on the weight of the phase.

59. A liquid detergent composition for machine dishwashing, comprising, in addition to further optional detergent ingredients for optional use,

d) from 10 to 90% by weight of pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate, and

e) from 10 to 90% by weight of one or more nonsurfactant, water-soluble, liquid binders,

f) from 0 to 40% by weight of water.

60. The composition as claimed in claim 59, which comprises, as nonsurfactant, water-soluble, liquid binders, one or more substances from the group consisting of polyethylene glycols and polypropylene glycols, glycerol, glycerol carbonate, ethylene glycol, propylene glycol, and propylene carbonate.

61. The composition as claimed in either of claims 59 and 60, which comprises, as nonsurfactant, glycerol.

62. The composition as claimed in claim 61, wherein said glycerol is present in amounts of from 10 to 80% by weight based on the composition.

63. The composition as claimed in claim 62, wherein said glycerol is present in amounts of from 15 to 70% by weight.

64. The composition as claimed in claim 63, wherein said glycerol is present in amounts of from 20 to 50% by weight.

65. A liquid nonaqueous composition as claimed in any one of claims 59 to 64, comprising, in addition to further, optional detergent ingredients,

f) from 20 to 50% by weight of pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate,

g) from 1 to 50% by weight of glycerol,

h) from 0 to 40% by weight of a polyethylene glycol which is liquid at room temperature, and

i) from 0 to 20% by weight of 1,2-propanediol

j) ≤ 2% by weight of free water.

66. The use of phosphates with nitrogen cations in detergents for machine dishwashing.

67. The use of phosphates containing exclusively nitrogen cations in detergents for machine dishwashing.

68. The use of pentaguanidinium triphosphate and/or penta[(3-amino-5-alkyl-1,2,4-triazol)ium] triphosphate in detergents for machine dishwashing.